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ANALYSIS AND PURIFICATION SECTION: SUMMARY OF ACTIVITIES JULY 1964 TO JUNE 1965

EDITED BY JOHN K. TAYLOR



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Technical Note 273

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ANALYSIS AND PURIFICATION SECTION: SUMMARY OF ACTIVITIES JULY 1964 TO JUNE 1965

Edited by John K. Taylor
Analysis and Purification Section
Analytical Chemistry Division
Institute for Materials Research

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FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964, reorganization. It consists at present of seven sections and about 85 technical personnel encompassing some 30 different analytical competences from activation analysis and atomic absorption to vacuum fusion and x-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition, it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is highly important. In addition, however, it has been my experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. At the National Bureau of Standards, such publications fit logically into the category of Technical Note. In 1965 we plan to issue these summaries for all of our sections. The following is the first annual report on progress of the Analysis and Purification Section.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

The Analysis and Purification Section of the Analytical Chemistry Division is engaged in two distinct yet complementary program areas. The first consists of research in six competence areas of analytical chemistry; namely, mass spectrometric gas analysis, polarography, coulometry, microchemistry, stoichiometry, and cryoscopy. The second encompasses projects in purification of research materials and may be classified as follows: distillation, ultrapure reagents, light-element purification, and other techniques.

In support of the scientific philosophy of the Analytical Chemistry Division, the section's total program has two objectives: (1) to provide analytical measurements of the highest reliability to the various research programs of the National Bureau of Standards and to the Standard Reference Materials Program, and (2) to develop new and improved methods of chemical analysis applicable to wide areas of materials research. The purification projects contribute directly to materials research by providing research materials for use by other investigators at NBS. At the same time, improved methods of purification are actively investigated.

This first annual summary primarily describes activities undertaken or completed during the period July 1, 1964, to June 30, 1965. Because this is an initial report, the research facilities of the section are described briefly to indicate its research and service capability. In addition, summaries of recent accomplishments of several programs are included where they will provide background material to illustrate the scope of the programs.

In order to specify adequately the procedures, it has been necessary occasionally to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

John K. Taylor, Chief
Analysis and Purification Section

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ANALYSIS AND PURIFICATION SECTION: SUMMARY OF ACTIVITIES
JULY 1964 TO JUNE 1965

Edited by John K. Taylor

ABSTRACT

This report describes the scientific programs and research activities of the Analysis and Purification Section of the Analytical Chemistry Division of the NBS Institute for Materials Research. Analytical research areas include: gas analysis by mass spectrometry, polarography, coulometry, microchemistry, stoichiometry, and cryoscopy. Research in methods of purification is concerned with distillation, high-temperature phase separations, and the ultra purification of chemical reagents. The facilities and general objectives of all programs are discussed. Research accomplishments described in some detail include: modification of mass spectrometer inlet systems to facilitate analytical sampling, polarographic analysis of lead alloys, coulometric calibration of micro-volumetric apparatus, precise analysis of copper in small samples, development of apparatus for the purification of inorganic fluorides by high-temperature phase separations, and development of an adiabatic calorimeter for determination of purity of volatile substances.

1. ANALYTICAL PROGRAMS

A. Mass Spectrometric Gas Analysis

The major interest in this laboratory is in the development and application of methods of gas analysis utilizing the mass spectrometer. Other instruments are available for use in conjunction with, or independent of, the mass spectrometer. The basic mass spectrometer has been extensively modified to facilitate the gas analysis function.

1. Instrumentation

The mass spectrometer most often used (see figure 1) is a Consolidated Electrodynamics Corporation Model 21-103C. This is a 180° magnetically focused instrument with electrostatic scanning. It is designed for the analysis of gases and highly volatile liquids, but the addition of a heated inlet system allows the analysis of less volatile liquids and solids. Samples of widely ranging chemical types and in any physical form are submitted for analysis. This variety of sample type as well as the variety of sample containers requires a sample handling

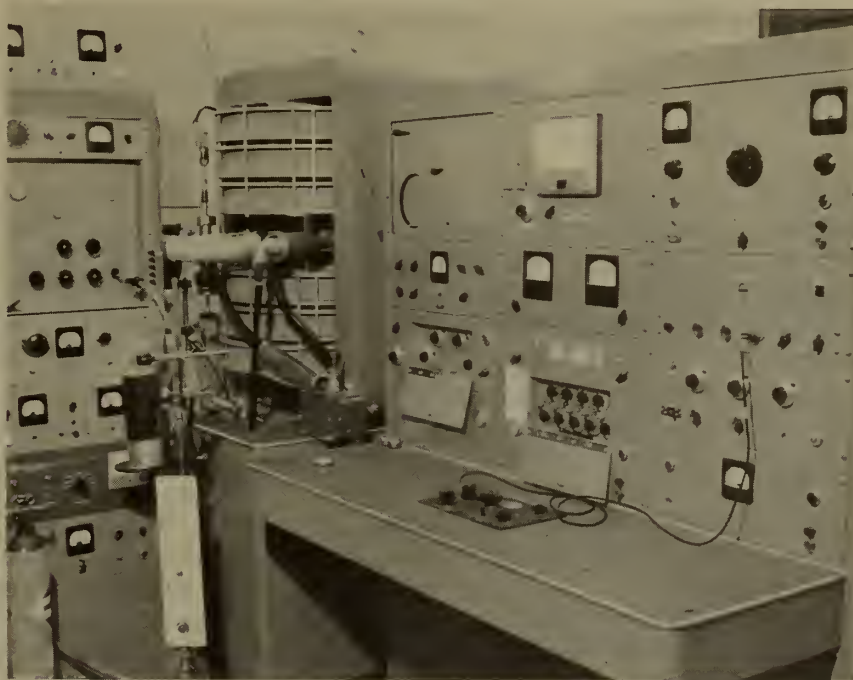


Figure 1. Analytical mass spectrometer.

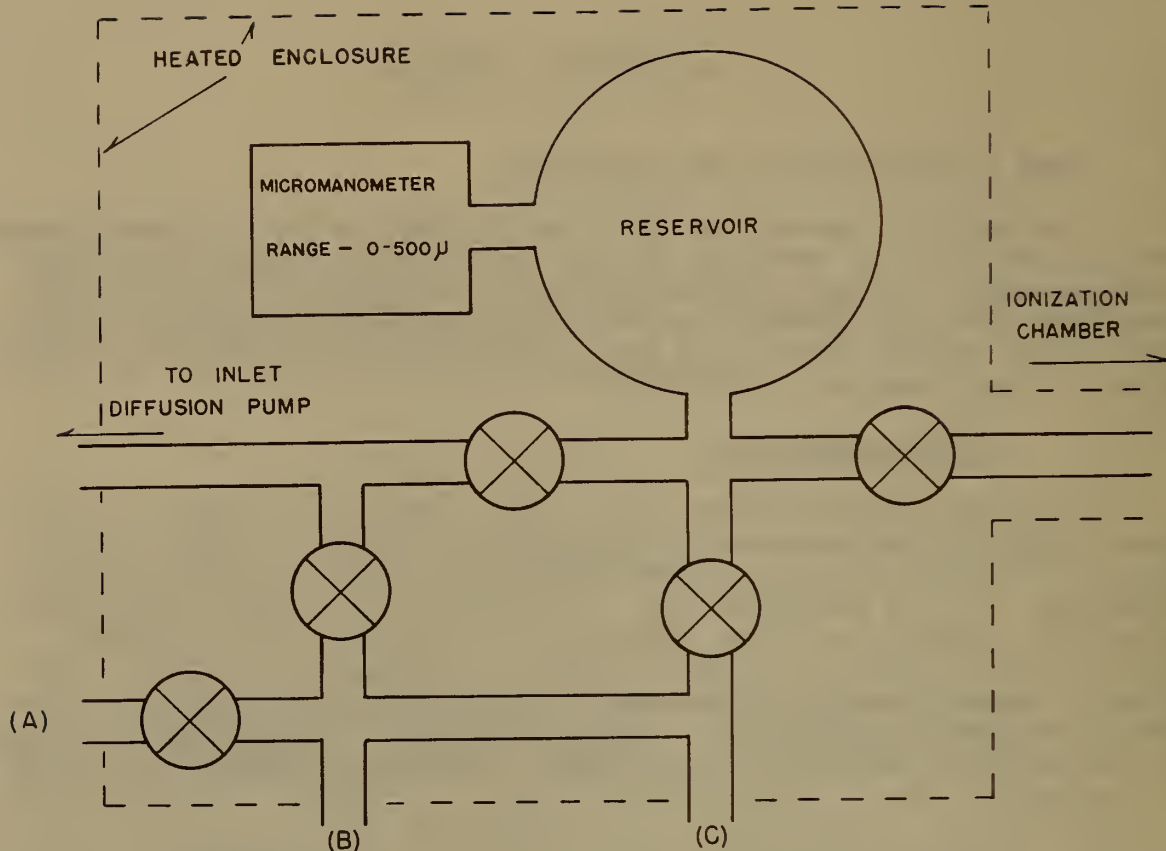


Figure 2. Schematic diagram of inlet system.

inlet system of considerable versatility. The original system has, therefore, been extensively modified to facilitate the analysis of all samples. A schematic diagram of the inlet system showing the arrangement of valves and inlet ports is shown in figure 2. Liquid samples of low volatility can be injected directly with a hypodermic syringe through the septum holder shown in figure 3, which is attached at (C) in figure 2. This holder was machined from a commercially available 12/30 taper, stainless steel outer joint. The threaded end was turned flat after the threads were cut to provide a seat for the rubber septum. The cap was machined from 3/4 inch stainless stock and can easily be finger tightened to provide adequate sealing. A furnace (see figure 4) is used to heat the entire assembly when samples of low volatility are injected. The furnace was built from a short length of brass tubing covered with glass cloth. The nichrome windings are held in place by a layer of asbestos. The thermocouple allows the temperature to be measured and adjusted to a value approximately that of the inlet system.

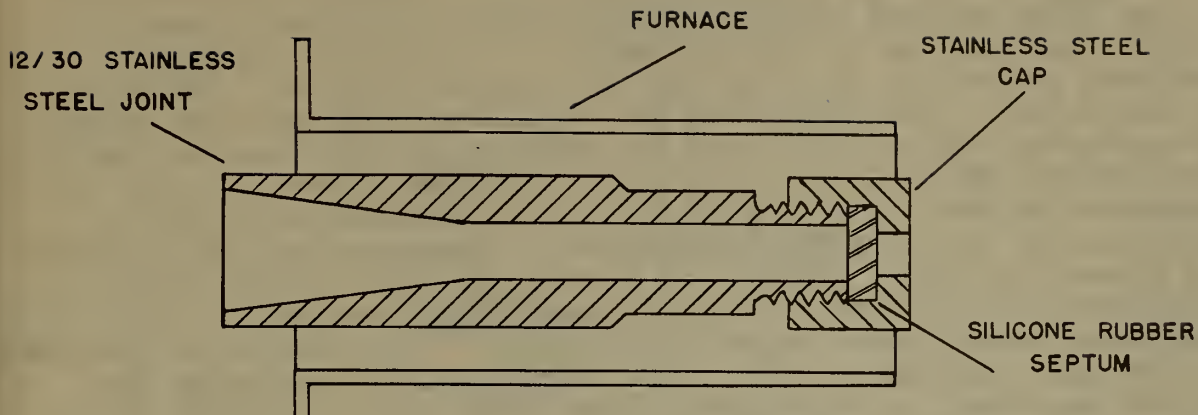


Figure 3. Septum holder for direct injection of liquid samples.

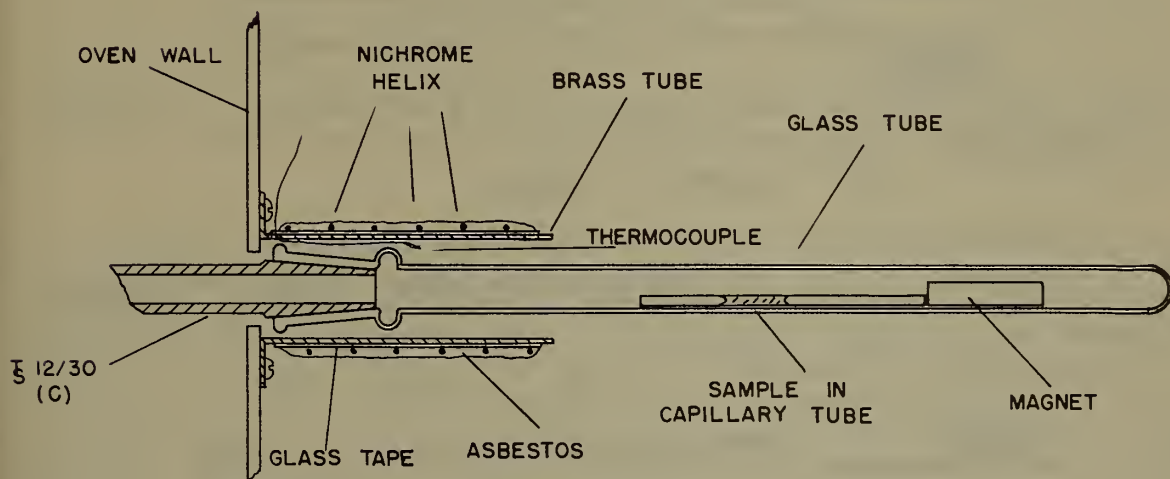


Figure 4. Device with furnace for introduction of solid and liquid samples of low volatility.

Samples of high viscosity and solid samples are admitted to the inlet system by the device shown in figures 4 and 5. Samples are placed in short lengths of capillary tubing and are then placed in the cool end of the glass tube. The tube is evacuated. The sample in the capillary tube is then moved forward with the magnet into the portion of the tube heated by the furnace where it is vaporized. In some cases, it may be desirable to seal the sample in a tube before evacuating to prevent loss of volatile components. These sealed capillaries are placed in short lengths of clean 1/4 inch copper tubing (figure 5A) which are attached to the inlet system at the stainless steel block shown in figure 6. This block is attached to the inlet system at (A). The copper tube containing the sealed capillary is evacuated after which the capillary is broken by bending the copper tubing. Ampoules or other large glass containers are treated in a similar manner using the device shown in figure 5B. Larger diameter tubing is connected to 1/4 inch tubing with reducing unions using either hard or soft solder. The sample tubes are broken by gently squeezing the large diameter tubing with a small C-clamp.

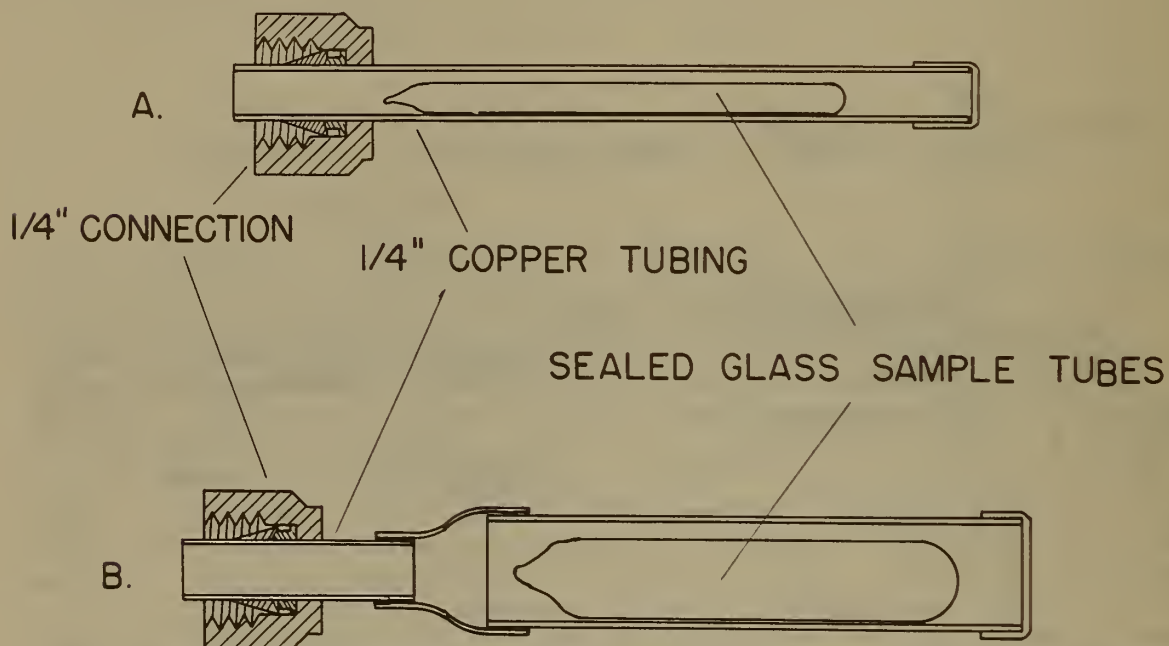


Figure 5. Device for introduction of samples contained in ampoules and sealed tubes.

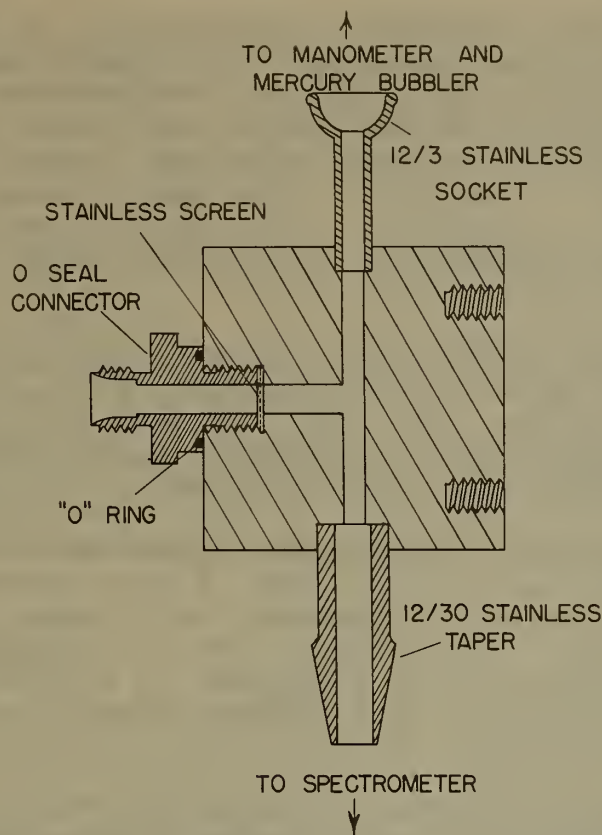


Figure 6. Block for direct connection to gas cylinder and for samples in glass tubes and ampoules.

Gases contained in flasks equipped with stopcocks or breakseals are attached to the inlet at (C) of figure 2. Those contained in lecture bottles or larger cylinders are attached to the O-seal connector of the stainless steel block shown in figure 6. Metal tubing is used for connecting cylinders to the system and the entire system can be evacuated as far as the cylinder valve. The manometer allows the measurement of sample pressure when the pressure is below one atmosphere. The mercury bubbler allows a slow flow of gas through this portion of the system thus eliminating contamination from small atmospheric leaks.

The outlet from the column of a gas chromatograph is connected to the inlet system at (B). Suitable valving has been provided to allow the condensation of compounds separated chromatographically for subsequent vaporization and admission to the inlet system.

A high-capacity mechanical vacuum pump has been connected to the inlet at (B) to allow very rapid pump-down of the inlet system and reservoir. In addition, it prevents excess contamination of the inlet diffusion pump, thus reducing the number of periodic shutdowns for pump cleaning. Also, the pump serves as a ready source of vacuum for the operation of a McLeod gage connected at (C) of figure 2. This gage is used to extend the range of pressure measurement in the reservoir from 0-500 μ to 0-10 mm.

The original vacuum system used to exhaust the ionization region consisted of a two-stage mercury diffusion pump with associated cold traps. This was replaced with a 15 l/s ion pump which resulted in a considerable saving in maintenance time and expenditures for refrigerants.

The original two-stage mercury pump is now used in parallel with the ion pump for the analysis of rare gases and in research on high-pressure mass spectrometry, both cases where the ion pump is inadequate. In addition, the availability of a second pumping system which can be activated in a short time has considerably decreased time lost during certain maintenance operations.

Minor changes in the electronics have been made to facilitate analyses. The only major change is the addition of a circuit to control and measure the ionization potential in the region from about 7 volts to 40 volts. The original available range of ionization potentials was from 50 volts to 100 volts. The circuit added is essentially that reported by H. E. Lumpkin [1] with minor changes.

In addition to the mass spectrometer, there is other equipment available for specialized gas analysis problems. An apparatus has been constructed for the accurate preparation of gas mixtures at pressures ranging from below one atmosphere to over a hundred atmospheres and with concentration of components as low as a part per million. These mixtures are used within the laboratory in research on analytical methods and for calibrating gas analysis instruments. Preparation of gas mixtures for other groups has been undertaken when such mixtures have not been readily available elsewhere.

2. Research and Development

The current research is concerned with a method of high-pressure mass spectrometry which will allow the determination of trace quantities (<0.01 mole percent) of components in gas mixtures.

At present it is necessary to concentrate impurities by physical methods if they are present at concentrations below the 0.01 mole percent level. This procedure is not only time-consuming, but because of the nature of the treatment, it introduces the possibility of seriously altering the composition of the sample.

The method under investigation consists of using sample pressures as much as two orders of magnitude greater than in normal routine operations. An evaluation is in progress of the change in nature of the spectra obtained at the higher pressures and of the effect of the changes on analytical problems.

The technique has been experimentally applied to several service problems with encouraging results, and it is expected that the technique will soon be applicable on a routine basis to any analysis requiring the detection of trace quantities of gases.

3. Analyses

In general, the major effort of the group concerns the qualitative and quantitative analysis of gas mixtures. These mixtures may range in complexity from relatively pure gases with one or two minor components to mixtures as complicated as pyrolysis products containing dozens of components. Simple mixtures with components at concentrations above 0.01 mole percent are quickly and easily analyzed. More complex mixtures with the same concentrations can be analyzed by employing specialized techniques such as fractional distillation, pre-separation by gas chromatography, and low ionization potential.

Requests for isotope abundance measurements are quite frequent. While the mass spectrometer employed here is not specifically designed for isotope-ratio measurements, such measurements can be done quickly and easily for a number of elements. The elements hydrogen, helium, boron, carbon, nitrogen, oxygen, and chlorine and their isotopes have been studied. Gas mixtures can be prepared and analyzed for components present at concentrations greater than 0.01 mole percent.

(E. E. Hughes and W. D. Dorko)

B. Polarographic Analysis

1. Introduction

Polarographic measurement is one of the most versatile analytical techniques that has appeared in the last 40 years. In principle, any material that is capable of electro-oxidation or -reduction and that can be dissolved in an aqueous or partially aqueous solvent can be polarographically determined. In many cases, the electrode process is sufficiently selective to tolerate the presence of constituents that would interfere in less selective methods. Otherwise, conventional separation techniques may be employed prior to the polarographic measurement. The high sensitivity of polarography when coupled with preconcentration procedures makes possible determinations at the nanogram level.

2. Facilities

The laboratory is well-equipped with both conventional and modified polarographic equipment.

Instruments covering the conventional range of polarography; namely, 10^{-2} to 10^{-5} M, are the Sargent Model XXI and the Sargent Model XV polarographs. The latter has accessory equipment consisting of a linear residual-current compensator and microrange extender to increase current sensitivity. The Oak Ridge Model Q1988A controlled potential and derivative polaroscan, shown in figure 7(b), lowers the sensitivity limit to at least 10^{-6} M. The controlled-potential mode of operation overcomes difficulties caused by large cell resistance; the derivative network allows increased resolution between closely occurring reductions.

The Sargent fast-sweep polarograph, shown in figure 7(c), for use with the hanging-drop electrode, further lowers the sensitivity limit to 10^{-9} M. By plating for a definite length of time into the very small volume of a mercury drop, a considerable concentration enhancement may be achieved. The current may then be measured as the reduced material is anodically stripped, resulting in significantly increased sensitivity.

The Davis Differential Cathode-Ray Polarotrace Model A1660, shown in figure 7(a), possesses normal, derivative, comparative, subtractive, and anodic-sweep modes of operation. Concentrations down to 5×10^{-8} M may be determined, preceding reductions in a ratio of up to 5,000 to 1 may be tolerated, and peaks differing by 40 mV may be resolved. In the twin cell mode of operation and by use of accurately known standards, precision



Figure 7. General view of polarographic laboratory.

of 5 parts in 10,000 may be obtained, which represents a 50- to 100-fold increase in precision over that obtainable by conventional polarography. By use of the reverse sweep, an amalgam electrode is formed during a 5-second delay period, which is then subjected to anodic stripping during the 2-second reverse voltage scan. This mode of operation permits the determination of reversibly reduced constituents in the presence of an irreversible reduction at the same peak potential.

3. Research and Development

Polarography has been especially suitable for a number of analyses connected with the certification of standard reference materials and with the analytical sample responsibilities of the section. In some cases, methods already reported in the literature were useful with few modifications, while in others, major development was necessary. Examples are mentioned only briefly. However, upon request, the section would be glad to furnish full details of all methods used or developed.

a. Standard Reference Materials. Polarographic methods for the determination of a number of elements in standard reference materials have proved highly advantageous, in particular for the analyses of cartridge brass standards for cadmium and tellurium and of white cast iron standards for lead, bismuth, and tellurium.

Cadmium was determined in approximately 1-gram brass samples in 0.1 N hydrochloric acid supporting electrolyte after removal of arsenic, tin, antimony, and copper by fuming with a hydrobromic acid-bromine mixture and electrolysis.

Lead and bismuth in the white cast irons were easily determined simultaneously by a method originally developed by Rooney [2]. Most of the iron was removed by an isobutyl acetate extraction of 1/5 or 2/5 aliquots of a hydrochloric acid solution of a 1-gram sample. After evaporation of the aqueous layer to dryness and dissolution of the residue in dilute hydrochloric acid, the residual iron was reduced with hydrazine hydrochloride. Ammonium hydroxide, sodium tartrate, and potassium cyanide were added, and lead and bismuth were extracted as the carbamate complexes with chloroform. The extracts were evaporated to dryness, and organic material was destroyed by evaporation with nitric and perchloric acids. The residue was dissolved in a supporting electrolyte of dilute nitric acid and sodium tartrate at a final pH of 4.5.

The determination of trace or greater amounts of tellurium in cartridge brass and white cast iron was conveniently done by cathode-ray polarography. Tellurium is separated from the cartridge brass by ammonium hydroxide precipitation using an iron carrier and determined with a cathode-ray polarograph in 1.5 M phosphoric acid. The results by forward scan are linear between about 0.05 and 0.7 to 1 ppm of tellurium in the final solution. Above this range, nonlinear peak currents are obtained, but by use of the reverse-scan mode of operation, the region of linearity may be extended to about 5 ppm. Tellurium is separated from the white cast irons by precipitation with sulfur dioxide using a selenium carrier and determined with a cathode-ray polarograph in 1.5 M phosphoric acid.

This work was described in a talk presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy March 1, 1965, and is being submitted for publication.

Antimony was also determined in the cast irons; however, the results obtained were not as satisfactory. The method of determination depended upon the amounts of antimony present. If the antimony content was greater than 0.1 percent, an aliquot equivalent to 100 mg of sample was reduced polarographically in a perchloric acid-hydrochloric acid supporting electrolyte after reduction of iron with ascorbic acid. Antimony in concentrations which were less than 0.1 percent was converted to the pentavalent state and extracted from a hydrochloric-citric-oxalic acid solution with ethyl acetate. After destruction of the organic material, antimony was reduced with sulfur

dioxide and determined in a sulfuric-hydrochloric acid supporting electrolyte. Although the precision of the results is generally good, further modification of the procedure is needed to increase the accuracy. A systematic study of methods of separation and investigation of other sources of error would undoubtedly result in an improved method. Among the possible sources of error are: incomplete antimony recovery of the large residues from some of the samples; loss of antimony through volatility; incomplete reduction of antimony to the trivalent state and incomplete oxidation to the pentavalent state at various steps of the procedure where it is required to be in a given oxidation state; and incomplete separation of antimony from some of the alloying elements of the cast iron.

b. Lead-Base Alloys. Nuclear magnetic resonance studies made by the NBS Metallurgy Division of alloys of lead with bismuth, indium, thallium, or cadmium to obtain information of their electronic structure necessitated the development of simple yet rapid methods for the chemical analysis of these materials, preferably requiring no prior separations. In general, 0.1 to 0.2 g samples were used for the analysis of the lead alloys. Smaller samples would have been adequate except for possible sample inhomogeneity.

In a series of lead-thallium alloys, the thallium composition varied from 1 to 76 percent. In some cases, both the lead and thallium content was needed as an indication of oxidation of the alloy. It was possible to determine both constituents directly in a 1 M potassium hydroxide supporting electrolyte measuring the thallium peak at -0.4 V and the lead peak at -0.7 V. The lead-bismuth alloys, ranging from 1 to 21 percent of bismuth, were analyzed in a sodium tartrate supporting electrolyte whose pH had been adjusted to 4.4. Lead could also be determined simultaneously if necessary.

For the determination of about 2 percent cadmium in a lead-cadmium alloy, lead was precipitated as sulfate, and aliquots taken from this solution were measured polarographically in an ammonia-ammonium sulfate supporting electrolyte.

The lead-indium alloys contained from about 0.005 to 23 percent indium. In these, lead was precipitated as sulfate, but not removed by filtration since its presence as sulfate did not interfere in the subsequent polarography of indium. The indium was determined in a supporting electrolyte which was 0.9 M in sulfuric acid and 1 M in potassium chloride. Both bismuth and indium could be determined simultaneously, in a similar way, in a ternary alloy containing about 1.2 percent bismuth and 0.7 percent indium. Bismuth was reduced at -0.1 V and indium at -0.7 V in a supporting electrolyte which was 0.9 M in sulfuric acid and 0.1 M in potassium chloride.

c. Miscellaneous. The rapidity of many polarographic determinations has resulted in the quick solution of many analytical problems encountered as a part of the analytical sample responsibilities of the section. Determinations of cadmium in several β -glucoheptonate cadmium bromide or chloride salts were made in a total elapsed time of approximately 10 minutes. The samples were dissolved in 0.1 N hydrochloric acid and measured polarographically at -0.7 V.

Cadmium was also easily determined in some cadmium chloride/potassium chloride-fused salts in a potassium chloride supporting electrolyte. The fused mixtures ranged in composition from 45 to 59 percent cadmium.

The synthesis of some metal organic phenanthroline compounds by the NBS Inorganic Materials Division in order to study their structure and properties required the determination of copper and zinc as well as carbon, hydrogen, and nitrogen. Generally, only a few milligrams of sample were available for all the determinations. Copper and zinc were easily measured simultaneously in an ammonium hydroxide/ammonium chloride supporting electrolyte.

Lead was determined simply and quickly in samples of tin pipe to be used for distilled water lines at the new Gaithersburg facilities. After dissolution and volatilization of the tin with hydrobromic acid and bromine, lead was determined in 0.1 M hydrochloric acid.

The mother liquor remaining after growth of ammonium dihydrogen phosphate single crystals was submitted for determination of trace amounts of arsenic. After reduction of As(V) to As(III) with hydrazine sulfate, arsenic was measured polarographically at -0.9 V in 1 N sulfuric acid. The polarographic sensitivity of this method is about 0.01 ppm in the final solution, corresponding to a limit of detection of 1 ppm in the 5-ml sample available for analysis.

At the request of the Bureau of Sport Fisheries and Wildlife, periodic analyses were made of copper and zinc in the local water supply to evaluate its suitability for use in the proposed National Aquarium. One hundred to 500-ml samples were filtered, the organic material in the water destroyed by acid treatment, and evaporated to dryness. The residues were dissolved in dilute hydrochloric acid and the solutions made ammoniacal. Copper and zinc were determined simultaneously on the cathode-ray polarograph from peaks appearing at -0.4 V and -1.2 V, respectively. By use of the sample sizes indicated, the method was applicable down to at least 5 ppb of copper and zinc.

A program of the NBS Metallurgy Division on defects and dislocations in metal single crystals required the determination of aluminum present in high-purity tin. The method used was similar to one developed by Rooney [3] for the determination of aluminum in cast irons. The tin matrix, which would interfere with the subsequent steps, was easily eliminated by evaporation with hydrobromic acid and bromine. When heated with the diorthohydroxyazo dye, Solochrome Violet RS, at a pH of 4.5 in a sodium acetate buffer, aluminum forms a complex which is readily reduced polarographically. Investigation of the sensitivity under these conditions showed that a linear calibration curve for aluminum could be obtained down to a final concentration of at least 0.02 ppm in the solutions measured. If a 1-ml final volume is used, this would represent 20 nanograms of aluminum. At these low concentrations, however, the aluminum blank derived from containers, the atmosphere, and the reagents used was found to be of the order of 0.015 ppm. Container blanks were minimized by the use of quartz and polyethylene. The use of redistilled bromine and hydrobromic acid resulted in no significant lowering of the 0.005 ppm blank from this source. The aluminum content of the high-purity tin samples had been expected to be in the 10-ppm range, but by use of this method, was found to be less than 0.2 ppm.

Investigation by the Harry Diamond Laboratories of the resistivity of some thin films of antimony and bismuth for possible applications such as electronic components required the analysis of very small samples. The films were formed by the evaporation of mixed powders in vacuum onto a coated glass plate. Since in some cases only as much as 0.3 mg of film was available for analysis, it seemed advisable to determine both the antimony and bismuth simultaneously if a supporting electrolyte could be found which would give well-defined waves for both. Investigation of conditions showed that both elements could be determined in a sulfuric-hydrochloric acid supporting electrolyte if the antimony were first reduced to the trivalent state with sulfur dioxide. The samples in question ranged from 4 to 70 percent of bismuth; however, the method developed is applicable to the range of 1 to 100 percent of bismuth.

(E. J. Maienthal)

C. Coulometric Analysis

1. Introduction

Coulometry depends upon quantitative electrolysis in which Faraday's laws of electrolysis are applied to chemical analysis. Accordingly, a coulometric analysis consists essentially of titrating with electrons. Although the electrochemical equivalency was quantitatively known for more than a century, its application to chemical analysis has been a development of the last 25 years and indeed largely of the last decade.

Coulometric analysis was first introduced into the program of the Analytical Chemistry Division in 1957. While most analysts prior to that time and even today have applied this technique to trace determinations or to determinations of ordinary analytical accuracy, the NBS has pioneered to develop apparatus, techniques, and procedures that provide assays of the highest precision and accuracy. Such determinations are based upon physical measurements which are easily made with high precision and accuracy. Moreover, the absolute nature of coulometric measurements is especially attractive since it minimizes the need for chemical standards in many cases.

The program since its initiation has been concerned largely with the exploitation of constant-current coulometry, and methods precise and accurate to a few parts per one hundred thousand have been developed for acidimetry and alkalimetry [4], for argentimetric titrations of halides [5], and for electroreduction of potassium dichromate [6]. A highly precise coulometer for integration of the current in controlled-potential electrolysis [7] has also been developed and described.

2. Facilities

High-precision constant-current coulometry is done with apparatus developed in this laboratory and shown in figure 8 and figure 9. The current is measured by comparison of the voltage of a saturated standard cell with the voltage drop produced across a standard resistor. The source of the current is a solid-state, constant-current supply that maintains it at a selected level to within a few parts in a million over a period of 8 hours. The output is monitored manually and is adjusted occasionally to compensate for drift. The time of electrolysis is measured with a quartz-crystal controlled time interval meter. This timer is calibrated with reference to Station WWV to provide time-interval measurements reliable to a part in a million.

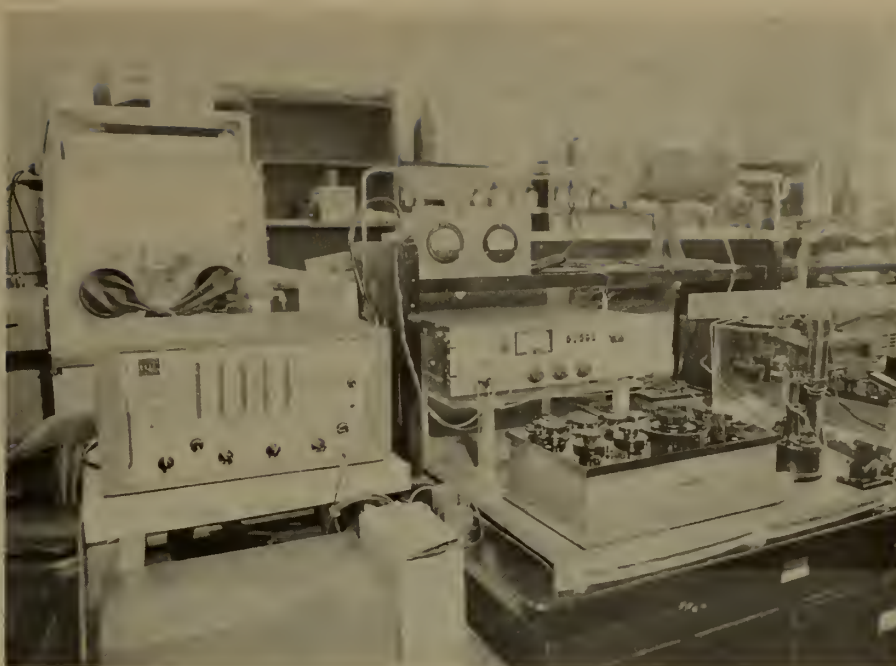


Figure 8. Equipment used in constant-current coulometric titrations.



Figure 9. Coulometric cell and associated equipment.

Measurements of mass are made on a microbalance so that a one-gram sample can be weighed to within a few micrograms. A calibrated mass is used in a substitution technique while repetitive weighings are made in a sequence designed to provide an average value of requisite precision.

The coulometric cell for high-precision analysis was designed in the early work [4] and is used with electrodes and end-point detectors suitable to a given determination.

Coulometric end points are determined in several ways, potentiometrically, amperometrically, or colorimetrically as the case may require.

For constant-current coulometric determinations where precision of a few parts in ten thousand is satisfactory, a commercially available constant-current supply is used incorporating a synchronous clock as timer. The latter is driven by a tuning-fork regulated power supply.

The section has a commercial model of the Oak Ridge Model Q2005 controlled-potential titrator.

3. Summary of Research

a. Determination of Uranium. A method of high precision has been developed for the assay of uranium in metal or in its compounds such as black oxide (U_3O_8). It consists in the reduction of uranium(VI) to uranium(IV) by coulometrically generated titanium(III). The electroreduction takes place in a 1 M titanyl solution in a 9 M solution of sulfuric acid at a current density of 2.5 mA/cm². Under these conditions, titanium(IV) is reduced to titanium(III) with essentially 100 percent current efficiency. The initial electrode reaction consists in the direct reduction of uranium. As the uranyl ion is depleted, electroreduction of titanium becomes the principal reaction, but the titanous ion in turn acts as reductant for the uranyl ion in the bulk of the solution.

Because the kinetics of the chemical reduction of uranium are unfavorable, it is necessary to overtitrate, to wait a sufficient period of time, and to determine amperometrically the amount of excess titanium(III) produced.

Full details of the method were disclosed at the EURATOM Conference on High-Precision Analysis of Substances of Interest to Nuclear Chemistry, January 18-22, 1965 [8], and will be published in the near future. In summary, analyses of uranium dingot metal and of standard oxide (U_3O_8) have shown an accuracy of ± 0.004 relative percent.

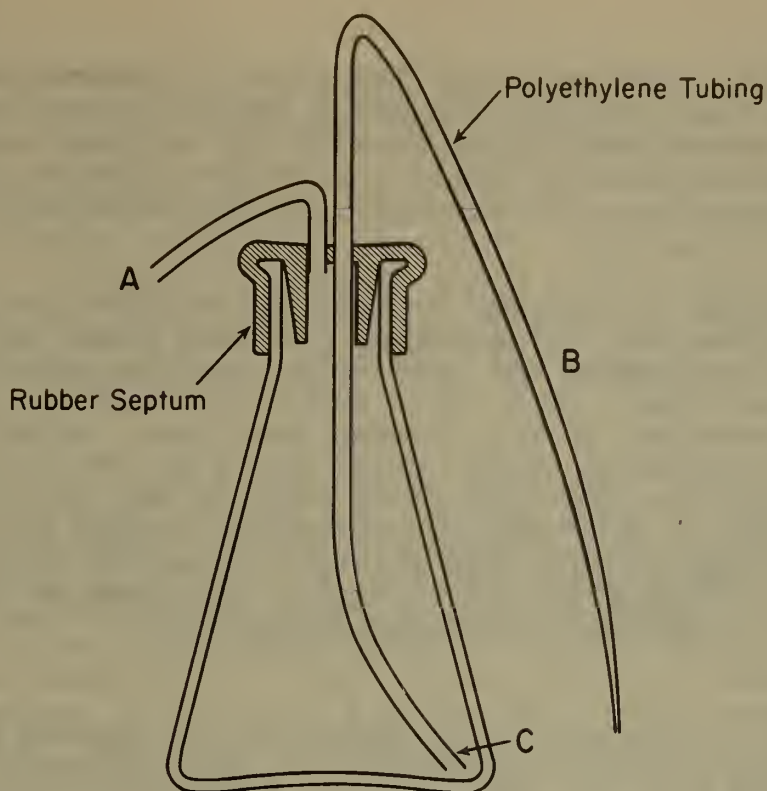


Figure 10. Apparatus for transfer of samples for coulometric analysis.

b. Liquid-Sampling Apparatus. Weighing considerations make a solid sample preferable wherever possible. In many cases, however, liquids or solutions must be analyzed either because of the nature of the sample or because chemical processing may be required prior to coulometric determination. The apparatus shown in figure 10 was developed to provide for quantitative transfer of liquids to the coulometric cell. A 125-ml Erlenmeyer flask, covered with a rubber septum, contains a sample which has been weighed by the technique described by Murphy in section E, page 25, of this report, or a solution resulting from chemical operations in situ. Two polyethylene tubes are inserted in appropriate holes in the septum as shown in the figure. The drawn-out tube serves to deliver the solution to the titration cell.

In use, tube B enters the cell through a suitable opening in the cover, and its tip is immersed in the electrolyte. Pressure is applied to tube A to transfer most of the contents of the flask to the cell where it is electrolyzed. At or near

the end point, suction is applied to A to return some electrolyte to the flask for rinsing which can be accomplished without disturbing tube B due to the flexibility of the connections. The rinsings are then returned for further electrolysis. The process is repeated, if necessary, before determining the final end point.

The apparatus also may be used to transfer solutions from a beaker to the cell for example. In this case, tube B is immersed in the beaker and suction is used to transfer the sample to the flask. The flask should be tipped to expose outlet C lest bubbling of air through the flask contents cause undesirable splashing on the upper parts of the vessel. The sample is then transferred to the cell as before. To minimize undue dilution of the sample by rinsing, it may be desirable to withdraw some of the cell electrolyte at the end point, transfer it to the beaker for rinsing, and return it to the cell for the final end-point determination.

c. Coulometric Calibration. A precise method has been developed for the calibration of microvolumetric ware by a coulometric titration procedure. The volumetric equipment is caused to deliver an accurately prepared normal solution of potassium dichromate into a coulometric cell where it is titrated using the precise method described earlier [6]. Calibrations at the 100- μ l level may be made with an accuracy of 0.1 percent while volumes as small as 1 μ l can be calibrated to 3 percent. Such calibrations are less difficult and more reliable than by gravimetry. Moreover, using the recommended technique of immersion of delivery tip, the method simulates the actual way in which such apparatus is ordinarily used.

The method was described at the 1965 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy [9] and has been prepared for publication.

4. Analysis of Samples

The highly precise methods of coulometric analysis developed in this section have found considerable use in analytical determinations of research samples for other sections. For example, the NBS Electrochemical Analysis Section has been engaged in isopiestic studies of solutions of calcium chloride and magnesium chloride. Reference solutions of this kind have been titrated with coulometrically generated silver [5]. Standard deviations of 0.01 relative percent are easily obtained on 1-gram samples of these solutions.

The method developed for the determination of uranium is being used to analyze uranium oxide (U_3O_8) for use as a standard reference material and to the assay of oxides of uranium for use in the preparation of isotopic abundance standards by the oxide dilution technique. Samples of approximately 0.5 g are analyzed after controlled ignition. Results obtained to date show a standard deviation of about 0.02 percent which is about double the value expected for samples of this size. The uncertainty reflects both analytical error and deviations from reproducible composition. More work is in progress to clarify this problem.

The high precision obtainable with small samples has made coulometry the method of choice for the assay of solutions of bromide and chloride for use in atomic weight determinations (see section E, page 26). In the case of bromides, samples of 2.5 meq were available for analysis in groups of four. The analytical uncertainty which included errors due to titration and sampling amounted to 0.007 percent in the concentration of the reference solutions. For the chlorides, samples of approximately 1 meq were provided, again in groups of four. The analytical uncertainty in this case was 0.02 percent.

(G. Marinenko)

D. Microchemical Analysis

1. Scope and Program

Microchemical analysis has been a valuable and much used tool in the research laboratory for many years because of its economical use of small samples and its relatively rapid determinations. Microchemical analysis in this section is concerned with the determination of major and minor constituents using samples of only a few milligrams. It includes both organic and inorganic materials. While the major emphasis has been on organic materials, there has been an increasing amount of inorganic work, especially with smaller samples.

The direction of the program is toward the analysis of even smaller samples (one mg or less). This is to be done through the development of more reliable and sensitive methods especially through the incorporation of instrumental approaches into the traditional elemental methods.

There has been a microchemical laboratory at NBS for approximately 30 years, and it has grown as the field has grown from the methods of Pregl and Emich to modern instrumental methods. The equipment in use is described below. Most of it is housed in one laboratory. A general view of one section of the laboratory is shown in figure 11. A second laboratory is used for wet chemical operations such as solution, heating, and fuming.

2. Microchemical Facilities

Three microchemical balances are in use. There is a Mettler M-5 microbalance and a noncommercial balance designed and constructed by Dr. A. H. Corwin of Johns Hopkins University. Both of these have a capacity of 20 grams and a sensitivity approaching 1 μ g. In addition, there is a Cahn electrobalance, which has a number of ranges. In the most sensitive range, 1 mg can be read to 0.1 μ g.

The determination of carbon and hydrogen is the analysis most frequently performed. A coleman carbon-hydrogen analyzer is used for most determinations of this kind. This is a semi-automated combustion apparatus in which the sample and absorption tubes are weighed, but all the other operations are automatic. The time required for a determination is about 20 minutes.



Figure 11. General view of microchemical laboratory.

A Sargent carbon and hydrogen combustion apparatus is used for materials which have special requirements of temperature, time, or tube packing. This apparatus is used for the combustion of liquid samples, especially those with high vapor pressures. Samples containing the alkali metals are burned in this apparatus because a flux is needed to prevent the formation of carbonates. In determining carbon and hydrogen in fluorine-containing compounds, magnesium oxide is added to the tube packing to remove the fluorine. The reaction is more efficient if the magnesium oxide can be kept hot continuously as it is in the Sargent apparatus. Each determination requires about 1 hour.

A Coleman nitrogen analyzer is used for most determinations of nitrogen. This is an automated instrument for the rapid determination of nitrogen by the micro-Dumas method. The weighed sample is placed in a combustion tube which is then attached to the apparatus. All manipulations are performed automatically as the instrument goes through an operating cycle of purge, combustion, and sweep. All gases except nitrogen are absorbed in an absorption vessel containing concentrated potassium hydroxide solution. The volume of nitrogen gas remaining is measured in a stainless steel syringe linked to a digital counter. Each determination requires 10 minutes compared with 1 hour for the Pregl method. The Kjeldahl method is used for some materials, especially for those materials low in nitrogen. The ammonia formed is determined by titration or if present in microgram amounts, photometrically.

For most determinations of sulfur and halogens, the oxygen flask method is used for combustion followed by titration with a suitable 0.01 N reagent solution. Occasionally, the Carius sealed-tube or the catalytic combustion-tube methods are used followed by gravimetric determination. A Cotlove-type coulometric titrator is used to determine small amounts of chloride or bromide (1 to 500 ppm). Fluorine when present below about 30 percent can be determined using the oxygen flask combustion. Larger amounts are determined by titration with thorium nitrate solution. Smaller amounts are determined spectrophotometrically.

Above 30 percent fluorine and especially in the perfluoro polymers, two problems arise: there is incomplete decomposition of the sample and the accurate determination of relatively large amounts of fluorine is difficult. Solution of these problems is among our aims.

A variety of methods are available for the determination of other elements and functional groups. Alkali metals and alkaline earth metals are usually determined by flame photometry although they can also be determined gravimetrically. Some metals such as copper, silver, zinc, and cadmium are determined by electrodeposition on small, weighed electrodes. Other elements such as iron, silicon, chromium, and phosphorus are determined photometrically although phosphorus is often weighed as ammonium phosphomolybdate after the destruction of organic material by Kjeldahl digestion.

3. Analytical Activities

A large part of the work involves elemental analyses of organic materials or compounds for other laboratories at NBS or for other government agencies. While these are mostly determinations of carbon, hydrogen, nitrogen, sulfur, and halogens, quite a few are of an unusual nature involving special handling or the development or modification of a method. An example is the analysis for small amounts (20-80 μ g) of chloride in polymers where the chloride is in a terminal position and an accurate analysis is needed for estimating the molecular weight. The chloride is determined after combustion by a careful titration with dilute standard mercuric nitrate solution. As another example, mercury in organic compounds is determined by burning the sample in a combustion tube and collecting and weighing the volatilized mercury on gold foil. Silicon in organic compounds is oxidized by a sodium peroxide fusion in a micro-Parr bomb, followed by conversion to yellow silicomolybdic acid which is measured photometrically. Trace amounts of chloride and iodide have been determined in photographic films and solutions. After removal of bromide and iodide, chloride is found turbidimetrically. Iodide is oxidized to iodate with sodium hypochlorite and then determined polarographically.

Certification analyses were made for the new cystine micro-chemical standard No. 143b which had been prepared by Delmo Enagonio of this Division. The purity of the cystine was evaluated by several microanalyses comparing this material with a previously issued standard reference material sample of cystine. The results of these analyses indicate no significant difference between the two samples. Cystine is used as a micro-chemical standard for carbon, hydrogen, nitrogen, and sulfur.

Another type of micro sample frequently received for analysis is the unexpected deposit or corrosion product found on parts of equipment, often after there has been a failure. Identification of the product might aid in determining the cause of the failure. A number of burned portions of aircraft have been examined to attempt to determine the source of the combustion products. This is of special importance in determining whether a fire occurred before or after a crash. Residues on engine parts have also been investigated. The material on the outside shell of a small electrical capacitor from a space missile was identified as electrolyte which had seeped through a tiny failure. Identification of the corrosion product on a naval mine which had been in the Caribbean Sea for some time indicated that the part should have been of a different metal. Analyses have also been made of the solid combustion products often found in the fluorine oxidation bombs used in calorimetric measurements.

A number of analyses have been concerned with determination of trace impurities in water. Samples of water have been received from the future National Aquarium where the interest is in the part-per-million amounts of copper and zinc which are injurious to fish. Waste water from the National Airport has been analyzed to aid them in planning a water treatment plant. Reactor pool water from the Harry Diamond Laboratories was analyzed periodically for traces of sodium, potassium, chloride, mercury, aluminum, iron, rare earths, and solids to determine if the water purification system was working correctly. Drinking water from a government station in the Arctic was analyzed to determine the reason for its nonpotability; an excessive content of magnesium sulfate was found.

A number of unusual materials such as lithium hydride, lithium nitride, aluminum carbide, beryllium carbide, and boron carbide have been analyzed for the NBS Heat Measurement Section. This section, in determining calorific values, requires well-characterized materials if these results are to be meaningful. With most of these materials, the most meaningful is determination of the amount of gas evolved by acid treatment. Larger samples (200-300 mg) are used for these analyses.

In the case of beryllium carbide, it was found that the material was far different from the analysis supplied by the producers. In this analysis, which is typical of the group, beryllium carbide is dissolved in hydrochloric acid in a closed system. One mole of methane is formed from each mole of beryllium carbide present. The methane is swept through a drying column with air and then burned in a combustion tube packed with copper oxide. The carbon dioxide and water are weighed, the weight of carbon dioxide indicating the amount of methane formed and the amount of beryllium carbide originally present. Any excess of water over that which came from the methane is a measure of the amount of metallic beryllium in the sample. Free carbon remains undissolved in the solution and is filtered and weighed. Total carbon determined by combustion in an induction furnace and total beryllium determined gravimetrically give corroborative information of the beryllium carbide purity and make possible a calculation of the beryllium oxide present in the sample.

During the past year, the section has worked with J. C. Davis of the NBS Mechanical Systems Section in investigating the composition of antifreeze solutions used in the snow melting systems for aprons of aircraft hangars. Corrosion problems had arisen at a number of Air Force bases, but not at others. The investigation concerned the amounts and types of corrosion inhibitors present in the antifreeze solutions, especially those which showed the best inhibiting action. As a result of these analyses, specification have been developed to insure that the materials used will be satisfactory with respect to their corrosive action.

(R. A. Paulson and R. J. Hall)

E. Stoichiometry

1. Introduction

The composition of a chemical compound depends not only upon the impurities present, but also upon the stoichiometry; that is, the degree to which the compound conforms to the law of constant proportions. It is well known that deviations from ideal composition, nonstoichiometry, occur in many compounds. The degree of this departure from stoichiometry is often best detected physically by such methods as x-ray analysis. However, in many compounds, these deviations can be detected by precise chemical analysis as in $\text{TiO}_{0.7}$ - $\text{TiO}_{1.27}$; $\text{UO}_{3.0}$ - $\text{UO}_{2.67}$; and $\text{Fe}_{0.95}\text{O}$ - $\text{Fe}_{0.85}\text{O}$ (stoichiometric FeO probably does not exist).

Since there is the possibility of departure from ideal composition, stoichiometric considerations are necessary wherever highly precise chemical analyses are undertaken. Work in this section has been concerned with developing precise and accurate methods of analysis for the chemical elements to verify the stoichiometry of a compound to about 0.01 percent. Emphasis has been given to the Division's program for the mass spectrometric determination of atomic weights in which it is necessary to quantitatively blend the separated isotopes of an element with a precision of about 0.01 percent. Since the amounts of separated isotopes available for this use ordinarily are relatively small, the methods developed for their determination should require only small samples.

It is anticipated that future work will be focused on stoichiometric compounds usable for this program, but attention will also be given to stoichiometric problems arising elsewhere within the Bureau.

2. Research and Development

a. Precise and Accurate Sampling of Solutions. Mixtures of separated isotopes for calibration of mass spectrometers may be prepared by blending weighed amounts of each isotope in elemental form of known purity or in combined form of known purity and stoichiometry. They may also be prepared by mixing weighed portions of solutions whose concentrations are accurately known. The method of mixing weighed portions of solutions has the advantage of eliminating problems concerned with the homogeneity and the weighing form of the sample of separated isotope (hydrolysis, hydration, etc.). The problem of purity is also considerably reduced since it is not necessary to know the concentration of all the impurities present, but only the concentration of those impurities which would react chemically in the same manner as the element being studied.

The following method has been developed for the precise and accurate sampling of solutions. A solution of the material to be analyzed is placed in a 100-ml volumetric flask whose neck has been cut off so that only about 1 cm remains. The solution is diluted to about 65 ml and thoroughly mixed by swirling the flask for several minutes. The flask is sealed with a rubber septum and allowed to stand overnight in the case of a semi-microbalance to insure thermal equilibrium. The flask and contents are then weighed on the balance to ± 0.02 mg. Samples are taken from the flask by inserting a platinum or stainless steel needle attached to a glass hypodermic syringe through the rubber septum, withdrawing the desired amount of solution, and transferring it to a suitable container. A second needle which just punctures the septum serves as a vent. The syringe and needle are washed with distilled water and the washings combined with the bulk of the sample. The weight of the sample withdrawn is determined from the weight of the flask before and after the withdrawal of solution.

This system of aliquoting solutions is used to take advantage of the precision and sensitivity of a semi-microbalance. To do this, it is necessary not to exceed the 100-gram capacity of the balance. A glass weight buret could not be used because of its excessive weight. On the other hand, the cut-off, 100-ml volumetric flask, stopper, and 65 ml of solution weighed less than 100 g. Five to 10 grams of solution can be weighed to better than 1 part in 100,000 by this procedure.

b. Precise Methods of Analysis. Precise methods of analysis have been developed for the following elements.

(1) Chlorine. The chloride-ion concentration in solutions of sodium chloride containing negligible amounts of other halides and pseudo-halides has been determined by constant-current coulometric titration with silver ions generated at a silver anode. The end point was determined amperometrically. Samples containing approximately 1 milliequivalent of chloride ion were analyzed with a standard deviation of about 0.02 percent. The results of this work were applied to the mass spectrometric determination of the atomic weight of chlorine [10].

(2) Bromine. The bromide-ion content of solutions of purified sodium bromide containing negligible amounts of other halides and pseudo-halides has been determined by constant-current coulometric titration with electrogenerated silver ions in a manner similar to that described for chloride ion. Samples containing about 2 milliequivalents of bromide ion were analyzed with a standard deviation of about 0.01 percent. The results of this work were applied to the mass spectrometric determination of the atomic weight of bromine [11].

It is usually necessary to chemically purify the separated isotopes to insure removal of those elements that would interfere with the mass spectrometric measurements or with the analytical method. The bromine isotopes (as NaBr) were purified by a method developed previously in this section, based on the preferential oxidation of bromide to bromine with dilute nitric acid [12]. This purification was necessary to insure the removal of the other halides, iodide, and chloride, and the pseudo-halides, cyanide, and thiocyanate which would react with silver to form insoluble compounds and cause the determination of bromide to be in error. About 0.1 percent of chloride ion was found to be originally present in the separated bromine isotopes, which would have caused an error of 0.2 percent in the bromide determination if it had not been removed. The purification procedure reduced the chloride concentration to less than 0.001 percent.

(3) Copper. A method requiring small samples has been developed for the precise assay of metallic copper and its solutions. The method is based on the electro-deposition of the copper onto a small platinum electrode. The gauze cylinder of this electrode is 1.5-cm high and 2-cm in diameter, and weighs about 1 gram. A 6-dram vial serves as the electrolysis cell. The assembly is shown in figure 12.



Figure 12. Microcell for electrogravimetric determination of copper.

The copper remaining in the electrolyte after electrolysis is determined spectrophotometrically with sodium diethyldithiocarbamate. Using high-purity copper as a reference material, it has been shown that samples containing 0.10 to 0.25 grams of copper can be assayed with a standard deviation of 0.007 percent. The results of this work have been published in Analytical Chemistry [13] and have been applied to the mass spectrometric determination of the atomic weight of copper [14]

(4) Chromium. A precise method for the determination of chromium has been developed. In this method, trivalent chromium is oxidized to hexavalent chromium by hydrogen peroxide in alkaline solution and the excess oxidant is destroyed. The hexavalent chromium is then determined by constant-current coulometric titration with ferrous ions generated at a platinum cathode by electroreduction of ferric ion. The end point is determined amperometrically.

The accuracy and precision of this method was determined by applying the procedure to NBS standard reference material 136b, potassium dichromate. This material has been shown to be 99.977 percent $K_2Cr_2O_7$ [6] based on oxidizing power. Four solutions of this material were prepared on a weight basis, and the concentration of each solution was calculated as milliequivalents of chromium per gram of solution. Four to six samples were withdrawn from each solution and the chromium in each sample was partially reduced with hydrogen peroxide in acid solution to simulate the conditions of the separated isotope solutions. The chromium in each sample was determined as described and the results were compared to the amounts known to be present.

Data resulting from these analyses showed that: (a) the average concentration of chromium for each set as determined by this method agreed to within 0.002 percent with the calculated concentration, and (b) the standard deviation of an individual determination (20 degrees of freedom) is calculated to be 0.010 percent for a solution containing 1.0 meq Cr/g solution. The excellent agreement between the average for each set and calculated amount of chromium also proved that the oxidation of trivalent chromium to hexavalent chromium by hydrogen peroxide in alkaline solution is quantitative and that the excess hydrogen peroxide is completely destroyed.

The procedure developed by this work is being applied to the mass spectrometric determination of the atomic weight of chromium which is now in progress.

(T. J. Murphy)

F. Cryoscopic Analysis

1. Introduction

The study of the change in temperature as a function of the change in ratio of the solid phase to the liquid phase in ideal or nearly ideal solutions is called cryoscopy. This temperature change is directly dependent on the initial purity of the system, consequently cryoscopy can be used as a highly sensitive tool for determining concentrations of impurity in these materials. Basic principles involved in estimation of purity by the cryoscopic method have been described in detail by Glasgow, Streiff, and Rossini [15].

The basic difference between the three most widely used cryoscopic techniques is the fashion in which the liquid-solid ratio is determined. In dilatometry, the ratio is observed as a function of volume; in the thermometric method (time-temperature freezing), the ratio is determined as a function of time; and in adiabatic calorimetry, the ratio is measured as a function of heat content. All of these methods are useful in obtaining precise and accurate determinations of purity if the heat of fusion of the material is known.

The thermometric method has been used extensively for years at NBS for determinations of purity in the range 99.0 mole percent up to 99.999 mole percent for many materials. an adiabatic calorimeter has recently been constructed and is presently undergoing final test. It will be used to further augment the Division's capabilities in the field of cryoscopy.

2. Thermometric (Time-Temperature) Cryometry

The thermometric system used at NBS consists of a glass sample container with a noble metal reciprocating stirrer. The detecting and measuring portion of the system is a platinum resistance thermometer, a d-c resistance bridge, and an automatic temperature recording system made up of a high-gain d-c amplifier and a potentiometric recorder. The cryometric cell is described in detail by Glasgow and Tenenbaum [16], and the measuring system is described by Ross and Dixon [17].

This cell can be operated as a closed system, open to normal atmospheric conditions, or under controlled atmospheric conditions. Since the closed system is constructed of glass and noble metals, it is useful in determining the purity of many substances which are toxic, reactive with air, or hygroscopic. If normal atmospheric conditions can be tolerated,

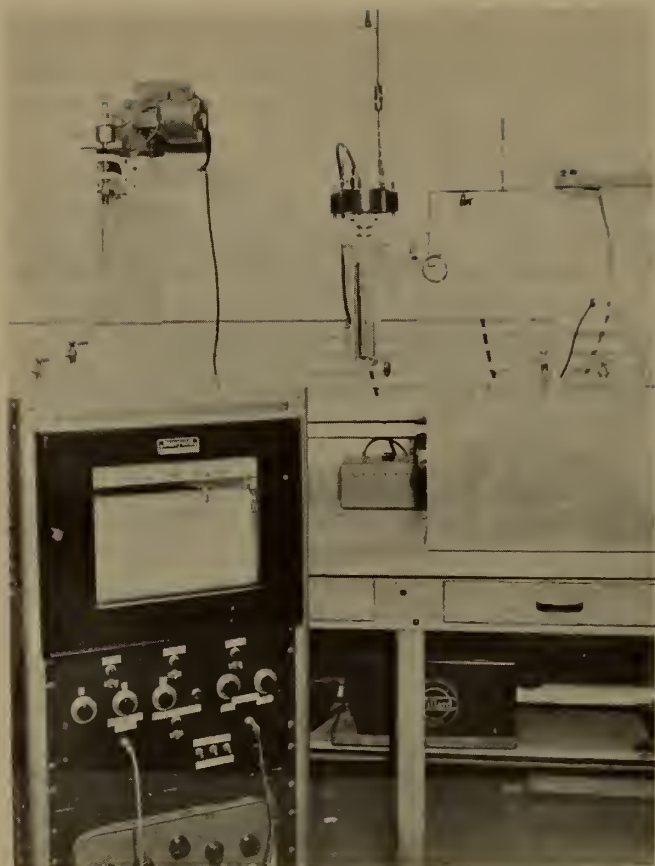


Figure 13. Thermometric cryometer and equipment for recording time-temperature cooling and melting curves.

the open system is easier and faster to operate than the closed system. The general temperature range of the equipment will accommodate substances which freeze between 150°K and approximately 350°K . The amount of sample required for a determination is about 50 ml. The time required to complete a single analysis varies from one-half to one day depending on the freezing temperature and whether open or closed system conditions are used. Figure 13 shows the time-temperature cryometer as it is normally operated.

The purity of highly purified samples of benzene, carbon tetrachloride, titanium tetrachloride, hydrogen chloride, dimethylphthlate, dichlorostyrene, isopropyl alcohol, and isomers of dichloroethylbenzene have been determined with this apparatus. The purity values of the presently available NBS standard reference materials of hydrocarbons were obtained by this method. Examples of more recent results and comparisons of this method against the other cryoscopic techniques have been published [18,19].

3. Calorimetry

The National Bureau of Standards extensive and expanding program of evaluating research and reference materials demands that prime consideration be given to estimation of the total purity. The best known instrument, which uses physical methods of analysis, for determining the total purity of a material is the high-precision adiabatic calorimeter. Moreover, the calorimeter is a versatile tool, not limited strictly to analytical uses. This allows it to play a major role in producing information on physical constants and properties of research materials.

Since apparatus of this type is normally not commercially available, a program was initiated to design and construct a high-precision adiabatic calorimeter with special emphasis directed to extending the capabilities of the Division in evaluating the purity of materials. In general, the reliability of this type of apparatus is determined by its ability to ascertain true equilibrium temperatures and maintain precise adiabatic conditions. Accordingly, much effort has been devoted to the design and the construction of a sample container to achieve thermal equilibrium conditions. Fully automatic temperature control units are employed to obtain precise adiabatic control.

Figure 14 is a cross-section sketch of the calorimeter construction. The sample container, valves, and filling assembly are made of platinum, iridium, and gold to minimize heat transfer problems and to provide a surface which is inert to a broad range of materials. Perforated disk-type vanes of platinum are horizontally attached from a central re-entrant well to help prevent segregation of impurity during analysis. The sample container is suspended in the calorimeter by a thin-walled platinum tube containing a needle valve to allow sealing of the sample container. This prevents vaporization of material into the filling tube during analysis. The central re-entrant well contains a platinum resistance thermometer and a non-inductively wire wound heater.

A copper shield surrounds the sample container. Electronic equipment controls the shield heaters so that the temperature can be automatically maintained the same as that of the sample container. Thermocouples between the shield and the sample container control operations of the electronic equipment. The space surrounding the shield and sample container is maintained at a pressure of approximately 10^{-6} mm mercury.

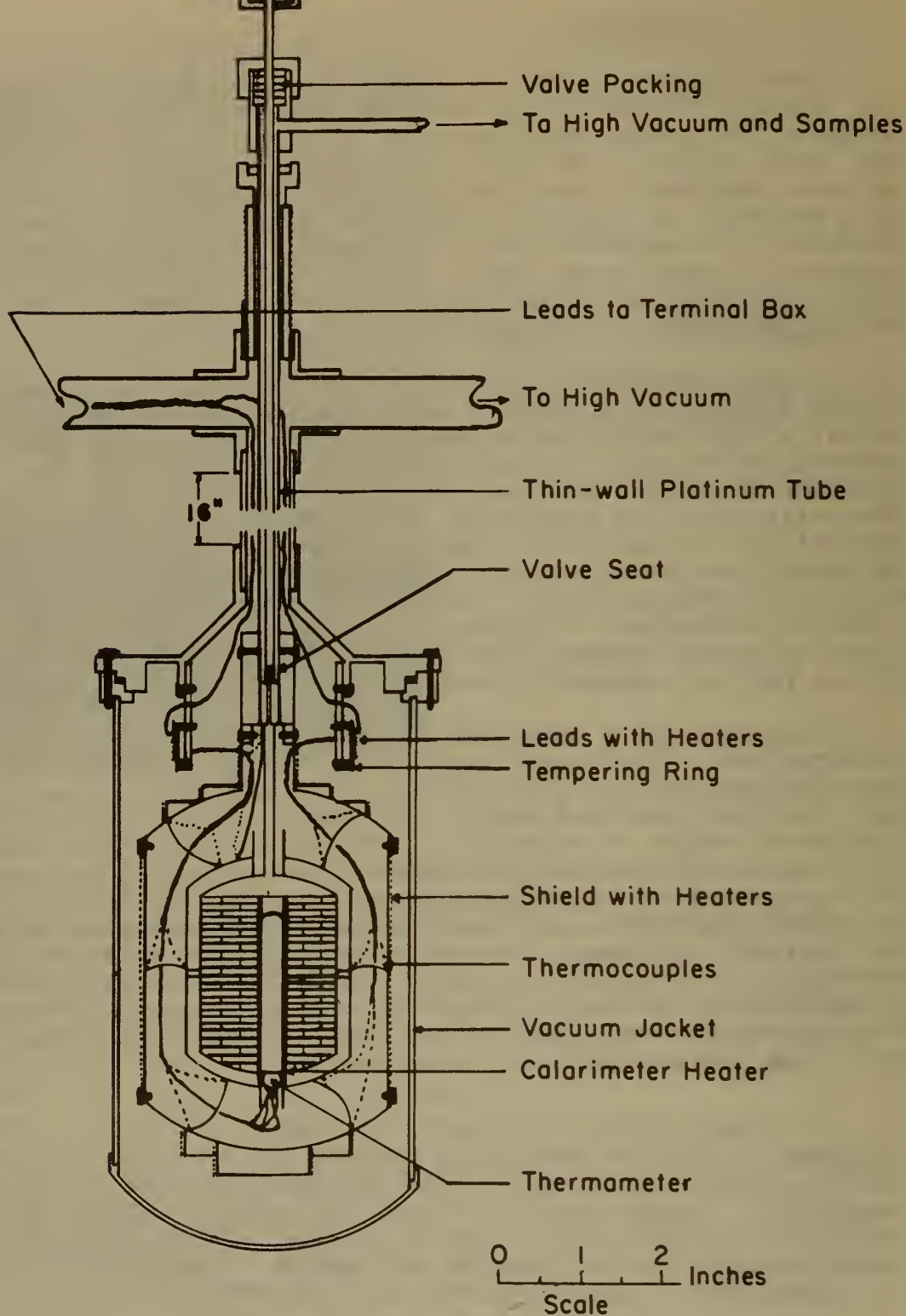


Figure 14. Adiabatic calorimeter for volatile materials.

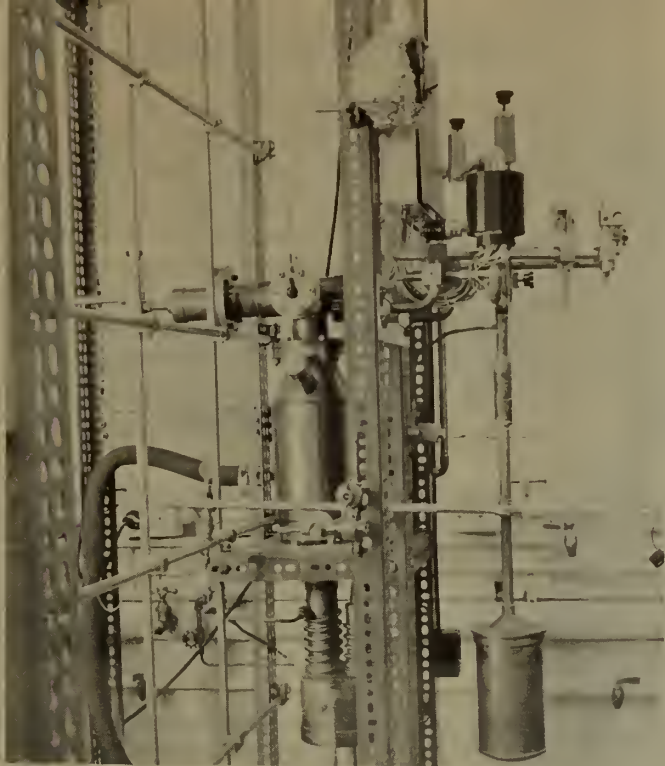


Figure 15. Calorimeter vessel attached to vacuum system.

The temperature control units operate from an amplified signal to an indicating potentiometric recorder with a control setting device. A control unit which automatically produces an output current proportional to the input requirements of the process completes the system. Direct current is used to avoid electronic interference that is normally associated with the use of alternating current. The temperature of the sample is measured with a platinum resistance thermometer and a Mueller G-3 bridge. Electrical input energy is determined from measurements taken with a six-dial, triple range potentiometer which provides precise measurements of voltages between the limits of zero and 1.6 volts. The time interval of heating is obtained by using NBS standard time frequencies and a gated electronic counter. The rise of the electrical input signal at the beginning of the heating interval starts the counter and the fall of the signal at the end of the interval stops the counter. A highly sensitive microvoltmeter is used as the detector for the bridge and potentiometer. A low pass filter is used to eliminate line interference to the detector from rectified d-c sources used to supply power to the main and shield heaters.

The calorimeter is mounted in a stationary position and is limited to the assaying of materials which can be introduced and removed by distillation. The temperature range of the system was designed for determining purity of materials which melt from 90°K to approximately 375°K .

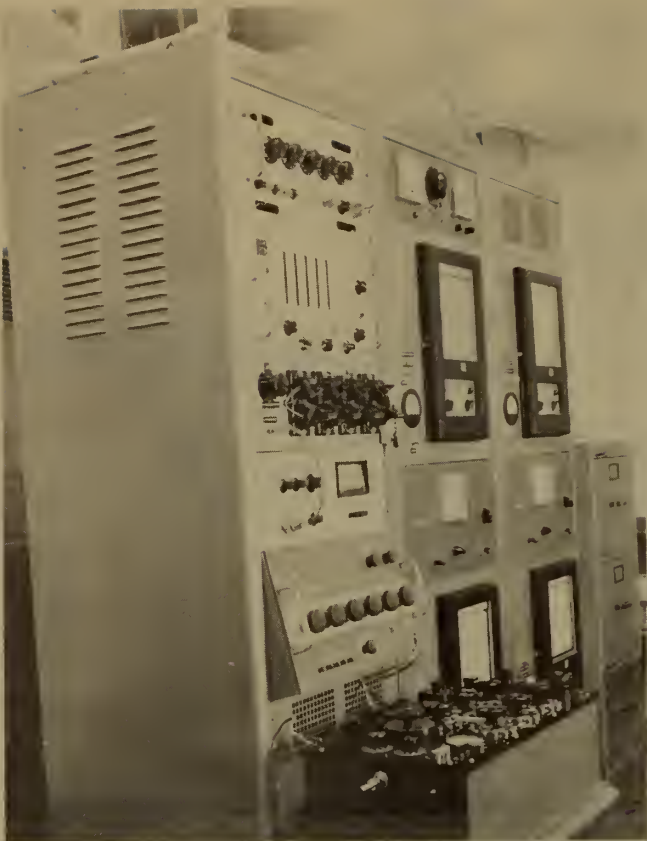


Figure 16. Temperature controls and measurement station for adiabatic calorimeter.

Three days to one week are required for the completion of a single analysis. Approximately 50 ml of sample is required, but the method is nondestructive and the material can be reclaimed. All the data needed for a purity determination can be obtained from one experiment.

Construction of the apparatus has been completed and the system is presently undergoing performance testing and calibration.

Since analyses have not been made with this equipment, no claims can be made regarding the precision and accuracy of its measurements. However, it is anticipated that a subsequent report will show that the analytical capability of this Division to estimate concentrations of impurities in the parts-per-million range by cryoscopic methods has been improved by an order of magnitude.

(H. D. Dixon)

G. Supporting Techniques

In the recent past, research projects have been active in the competences of gas chromatography, nuclear magnetic resonance spectroscopy, and infrared spectroscopy. While these programs are inactive at the present, the section has modern equipment of this kind and possesses considerable experience in its use in analytical applications. Thus, infrared and nuclear magnetic resonance spectra are prepared for other research groups. Gas chromatography finds extensive use both in the analysis of research samples and in monitoring purification processes and in evaluating the purity of the purified material.

The section also uses the above techniques in conjunction with other analytical competences. Thus, gas chromatography may be used as a preconcentration or preseparation technique to facilitate a later analysis by mass spectrometry. Infrared spectrometry is likewise used to identify fractions from gas chromatographic measurements.

In addition to providing analytical services with these techniques, the section maintains the equipment and makes it available to qualified users in other sections of the Bureau. This arrangement is especially advantageous to those chemists who have only occasional need for specialized equipment, but who are skilled in its use and are willing to devote the time necessary to make their own measurements and interpret the data.

(J. K. Taylor)

2. PURIFICATION PROGRAMS

A. Distillation

1. Introduction

The laboratory provides facilities for purification of research quantities of materials that are needed by the personnel of the Bureau of Standards. The distillation laboratory will attempt to purify any material whose vapor differs in composition from the liquid or solid phase. Since no one type of still is adapted to all the needs which arise, a variety of types have been set up hoping to anticipate the most likely requests. This is not always possible so that additions or modifications to the equipment must be made from time to time. Not only is the requirement for equipment unpredictable, but the workload varies so that automation is desirable to avoid variation in the requirement for personnel. Accordingly, the equipment has been designed and constructed in this laboratory to operate continuously for long periods of time with as little attention as possible.

2. Facilities

The types of stills which are now available are cataloged in table 1. The small stills are equipped with reflux controls, but samples of distillate are removed manually because the tubes which connect the sample receivers in automated collectors can lead to mixing through the vapors. However, distillate collects so slowly that personal attention is not an undue burden. Larger stills are equipped for the control of the rate of boil-up, reflux rate, and automatic collection of fractions in a closed system.

Figures 17 and 18 show some of the equipment in the distillation laboratory. On the left of (A), figure 17, is a cylinder which protects a large glass Dewar container for refrigerants such as solid carbon dioxide or liquid nitrogen. A pump circulates a cryostatic liquid through the refrigerant and thence to the head of the still for distillation of low-boiling materials. Solid carbon dioxide sufficient for 24 hours of operation can be placed in the Dewar, and by throttling the flow of the cryostatic liquid, the head of a small still can be cooled to any desired temperature as low as -50°C for long periods. By using liquid nitrogen, a temperature of -130°C can be reached. The consumption rate of liquid nitrogen is about 2 liters per hour.

Table 1. Description of laboratory stills

Type of Still	Quantity per Batch	Pressure of Distillation	Rate of Distillation for Good Results	Number of Theoretical Plates	Operating Temperature °C
	ml	mm Hg	ml/hr	Optimum Condition	
Micro-concentric tube	1-4	760-1	0.1	40	+250 to -190
Macro-concentric tube ^a	5-50	760-1	1-2	70-90	+150 to -190
Micro-spinning band (2 stills) ^a	5-100	760-1	1-2	70-90	+250 to -150
1-meter precision packed ^a	500-1500				+150 to +10
3-meter random packed ^a	1500-4000	760-90	15-20	200-260	+130 to +30
Oldershaw perforated- plate (30 stages) ^a	15,000- 20,000	760-300	1,000	10-25	+130 to +30
3-meter packed Monel ^b	500-1500	760-90	5-20	200	+250 to -190
Fused silica 1-meter packed ^c	200-1500	760-40	5-50	10	+1000 to -190
Molecular single stage	1-5	1-10 ⁻⁵	0.1-1.0	1	+400 to -190
Molecular falling film	25-50	1-10 ⁻⁵	5-15	1	+100 to +30
Molecular falling film with scraping blades	50-200	1-10 ⁻³	10-30	1	+150 to +30

^aReflux ratio controlled by timing mechanism^bReflux ratio controlled by throttling^cReflux ratio controlled by partial condensation

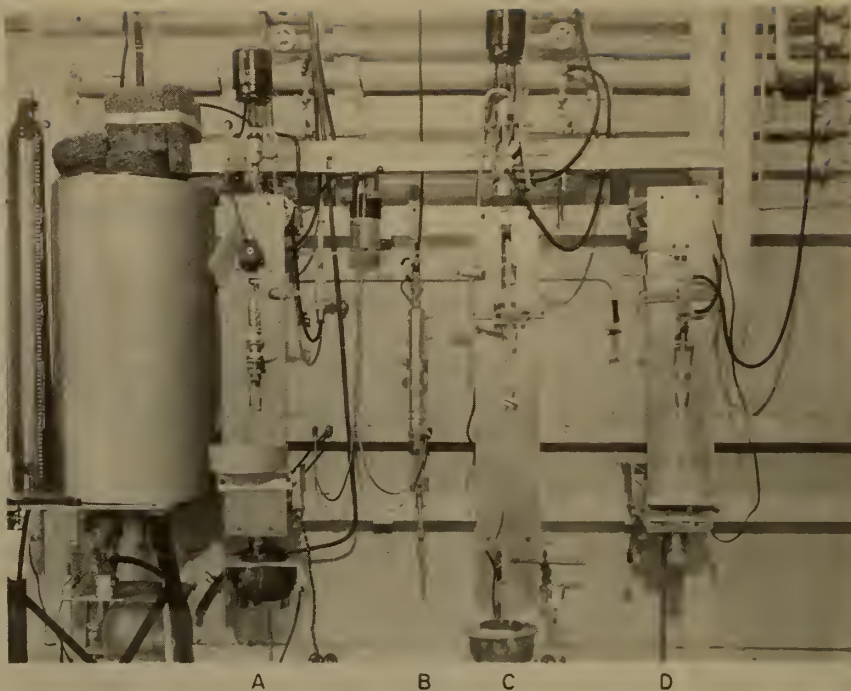


Figure 17. Small still equipment in the distillation service laboratory. (A) and (C) microspinning band stills with equipment for regulating temperature and pressure; (B) micro-concentric tube still; (D) macroconcentric tube still.

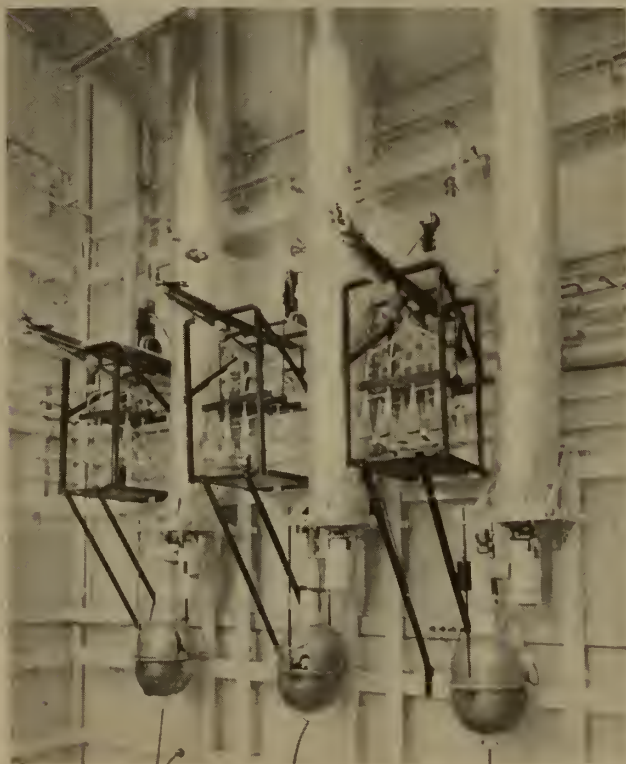


Figure 18. Three-meter by 25-mm packed stills with boil-up and take-off controls and closed-system fraction collectors.

Below the cylinder in figure 17 is a pressure control unit. Each still is regulated individually by one of these units. A detail of the control is shown in figure 19.

At the bottoms of the stills shown in figure 18 are the vaporizers. Details are shown in figure 20. The vaporizers are relatively safe for flammable materials because the heaters are enclosed in metal. Vapor from the flask rises through the large tube, passes horizontally to the left, and is emitted from orifice E to rise up the still column. Liquid returning from the column passes down through F and H and enters the flask at the side. If valve H is closed by a hand-operated permanent magnet, the column will fill with liquid for "preflooding." The wells D and G are for the insertion of thermistors to detect the rate of flow of vapor and to actuate a correcting mechanism to keep flow constant.

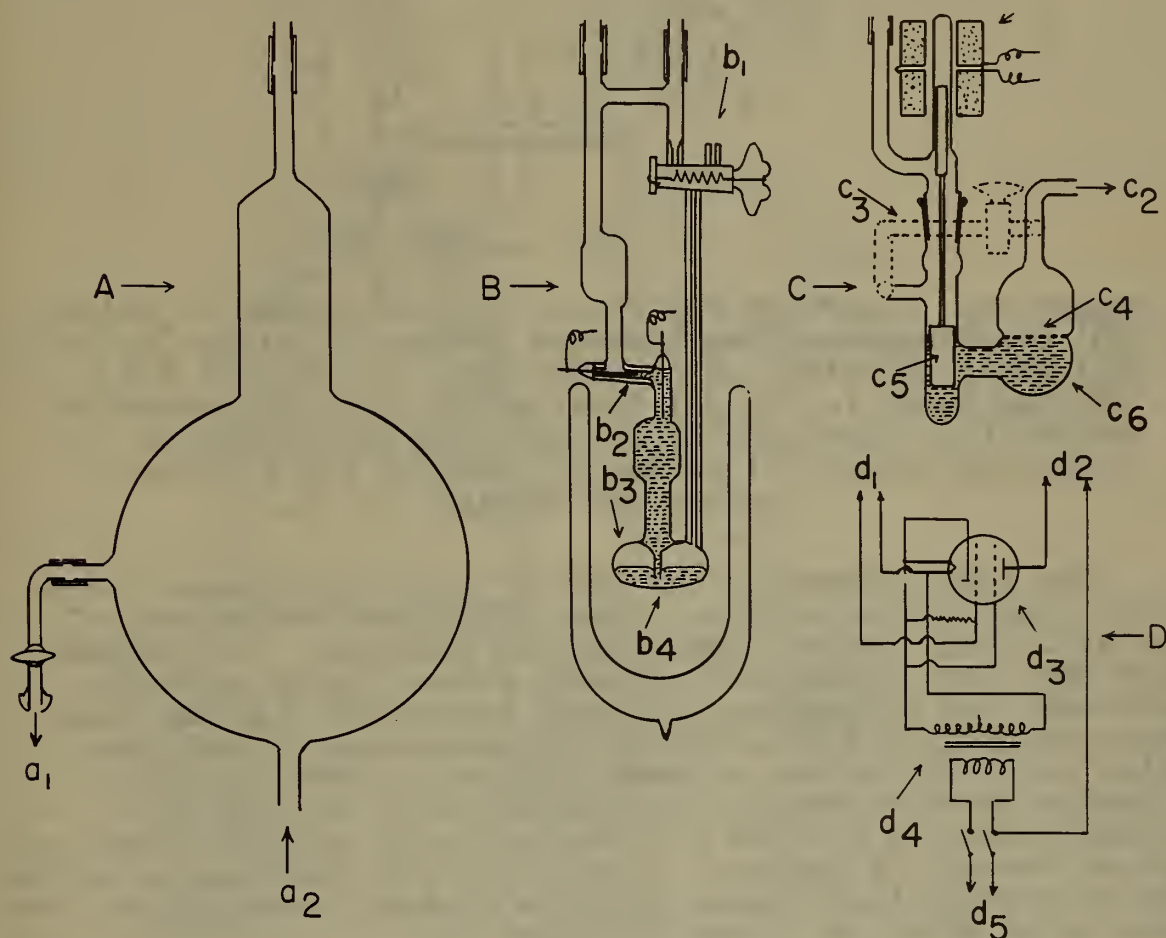


Figure 19. Pressure regulator. (A) ballast; (B) manostat; (C) vacuum control valve; (D) relay (lower case letters are detailed points of construction).

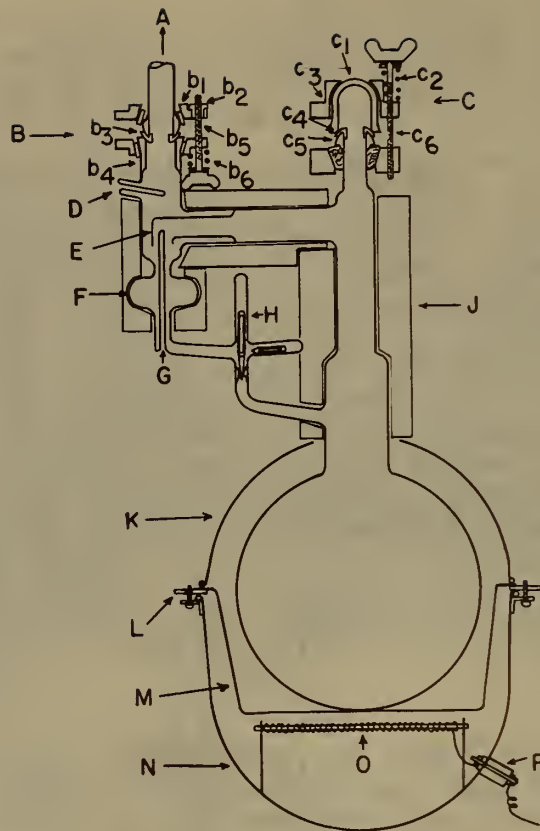
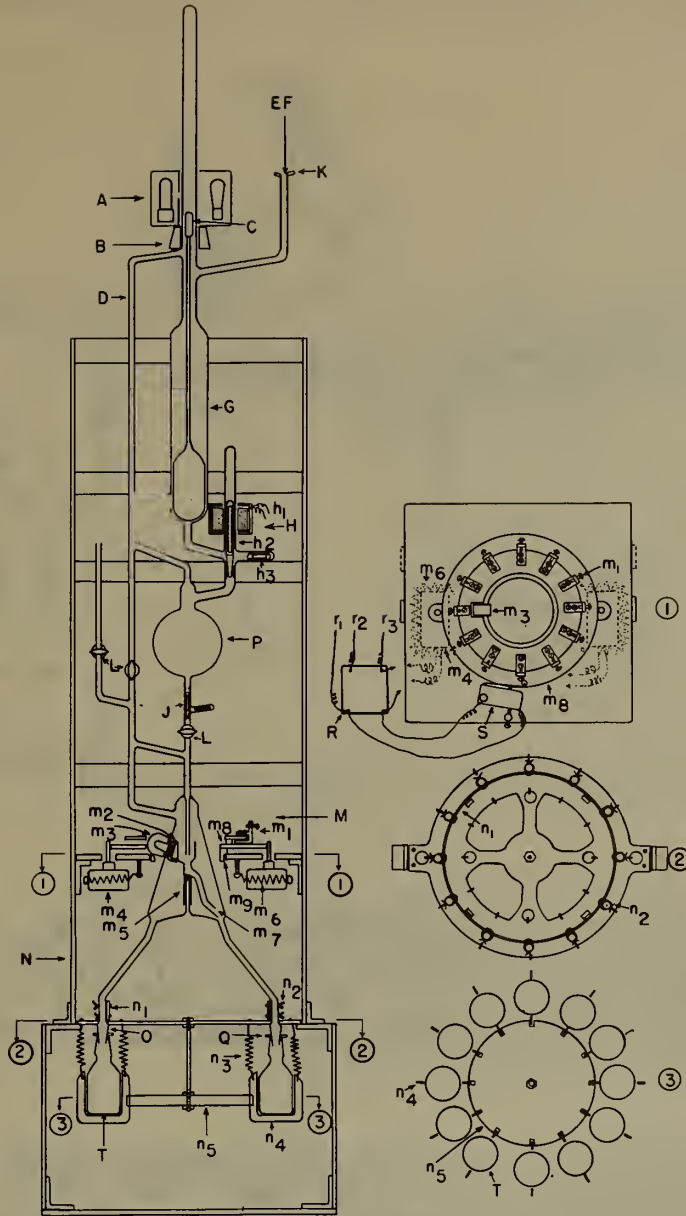


Figure 20. Vaporizer for still. (A) to column of still; (B) polyfluoroethylene gasketed spherical joint; (b₁ to b₆) detailed points of construction; (C) closure for filling tube; (c₁ to c₆) details (D) and (G) thermistor wells; (E) vapor nozzle; (F) bulb for measuring the returning liquid (H) valve; (J) through (P) details of heater and shield.

The metal frames at the left of each still support automatic fraction collectors. These units are independent of the stills and can be dismantled for cleaning. Two designs have been used. Figure 21 shows a rotary design with the photocell and preliminary receiver containing a glass float which actuates the collector. The units have 12 receivers which are inverted-cap bottles. Filled bottles can be replaced without disturbing the operation of the stills at reduced pressure and the bottles can be filled with inert gas before removal if desired. The collectors which are shown in the photograph (see figure 18) have sliding distributors, the details of which are shown in figure 22.

All the stills are assembled in units with tapered and spherical joints for ease of cleaning and repairing. Special polyfluoroethylene gaskets are used in place of greases.



FRACTION COLLECTOR

A photocell
 B cork support
 C glass bulb blocked within
 D pressure equalizer
 EF to head of still
 G receiver
 q_1 light weight glass float
 H solenoid valve
 h_1 magnet
 h_2 armature in glass
 h_3 "lock open" plunger
 J slow-leak valve
 K teflon gasketed joint
 L teflon lined stopcock
 M distributor
 m_1 adjustable stops

m_2 iron armature in glass
 m_3 permanent magnet
 m_4 6 watt, 10 rpm motor
 m_5 bearing for funnel
 m_6 spring pressing motor
 m_7 drain from funnel
 m_8 rotating disc
 m_9 bearing for disc
 N metal frame
 n_1 metal cylinder
 n_2 wire ties
 n_3 springs
 n_4 stirrup
 n_5 slotted disc
 O tapered joint
 P reservoir
 Q teflon gasket
 R delayed action relay

Scale 1/4
 r_1 hot 110 volts
 r_2 signal
 r_3 neutral 110 volts
 S microswitch
 T inverted stopper bottles

Figure 21. Rotating fraction collector. (A) through (T) detailed points of construction.

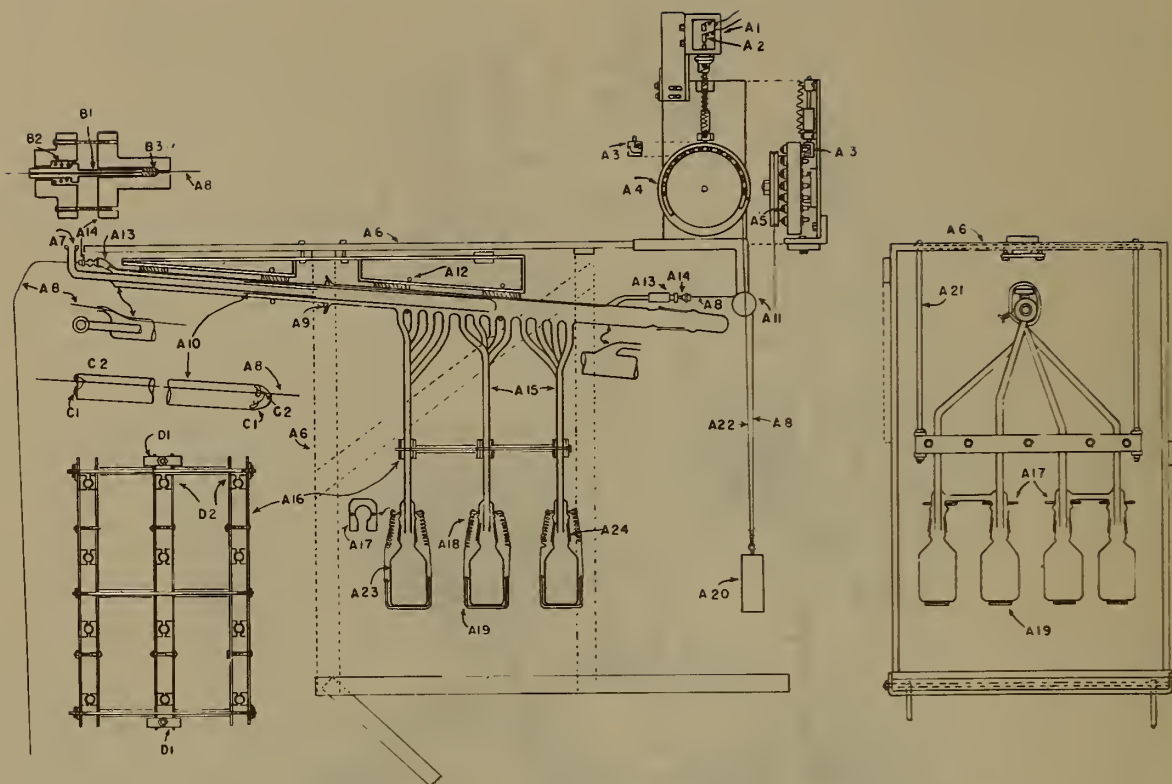


Figure 22. Sliding fraction collector. (A_1 to A_{24}) detailed points of construction of general assembly; (B_1 to B_3) details of packing glands; (A_{14}), (C_1), and (C_2) details of sliding sleeve; (D_1 to D_3) details of supporting frame.

Figure 23 shows the behavior of a 3-meter still packed with closely wound spirals about 2x2 mm. The graph shows that the effectiveness of separation (expressed in numbers of theoretical plates) increases gradually for about 50 to 75 hours after the column is filled with liquid distillate and drained (preflooded). Also, it shows that there is an optimum rate at which the column can be operated. For the mixture of n-heptane and 2,2,4 trimethylpentane which was used for the test, the optimum boil-up and through-put were 15 and 8 ml/min, respectively. The efficiency under these conditions reached about 220 theoretical plates. Expressed less technically, such a still can produce a mixture containing 97 percent n-heptane (bp 98°C) from a mixture with 2,2,4 trimethylpentane (bp 101°C) containing only 3 percent n-heptane.

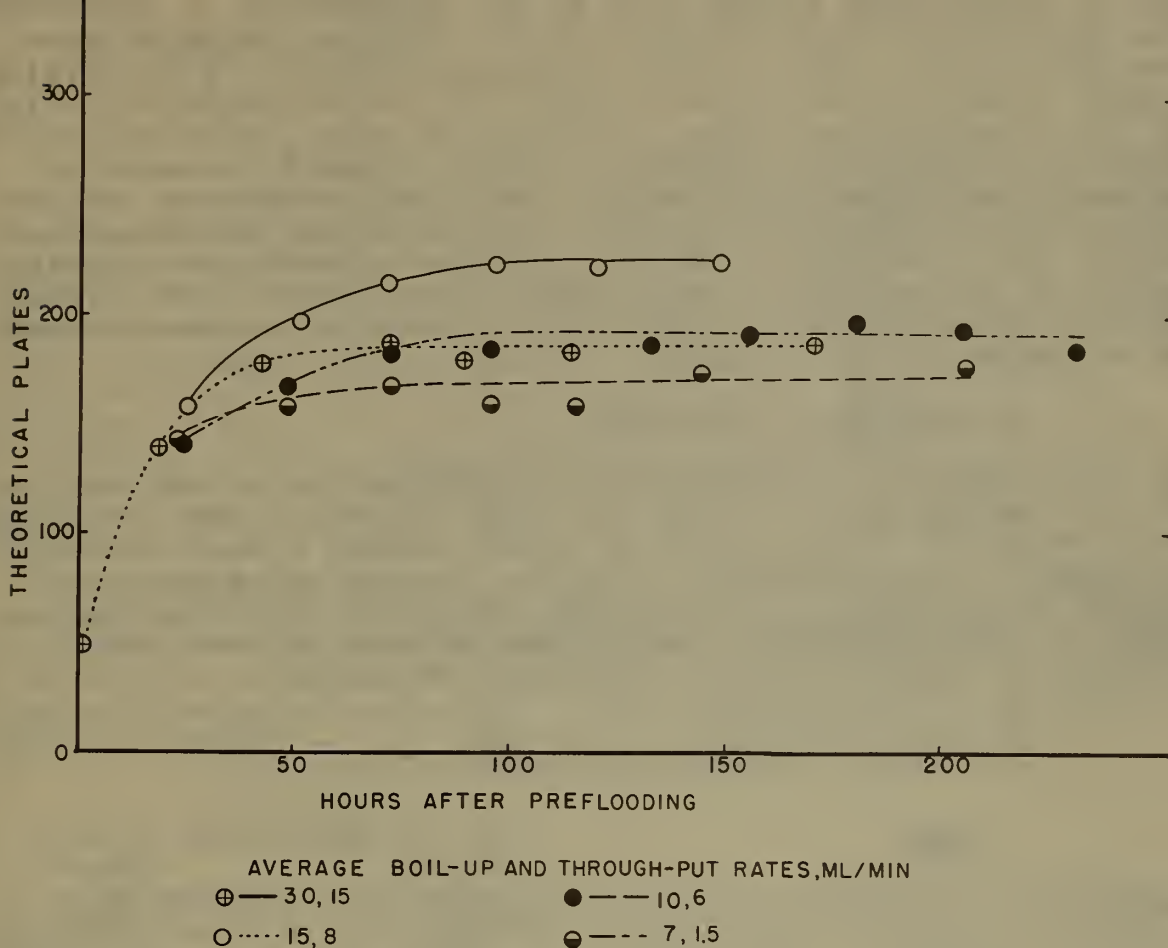


Figure 23. Efficiencies of 300-cm packed still columns at varying rates.

3. Research and Development

Stills which are equivalent to more than 200 theoretical plates are highly desirable but are not common. The simplest way to increase the total separating power is to increase the length of a column, but the improvement becomes smaller as the length is increased. It has long been known that a given column can sometimes be made more effective by using techniques other than simple rectification. For example, if a relatively nonvolatile liquid in which some constituents of a mixture are more soluble than others is flowed down a column during a rectification, the separation may be enhanced. The technique is termed extractive distillation and is somewhat analogous to gas-liquid chromatography (glc). To study the possibilities of extractive distillation further than has already been done, the effect of various extractive agents on the separation of test mixtures has been undertaken. The immediate purpose is to isolate a mixture of 2-methylhexane and 2,3-dimethylpentane

from an inexpensive source such as the heptane-cut of petroleum. This mixture is a good combination for testing stills of more than 300 plates. However, the long-range purpose is to develop a quick method of evaluating agents for extractive distillation and improving the technique of using them with laboratory stills. A micro spinning-band column has been modified to permit the continuous introduction of extractive agent at the top and removal at the bottom. The results are studied by glc examination of the distillate. This can be done without the complete removal of the extractive agent from the material. The effectiveness of an extractive agent for separating a given mixture can be evaluated in less than 24 hours in this way.

4. Purification Activities

The demand for purification by distillation at the NBS is somewhat irregular. With the equipment which has been described and a personnel of two, there is almost always a small backlog of requests. Over a number of years, requests have been most frequently for lots of 50 to 100 ml of material and boiling points of the material are most often between 50° and 100°C. More organic than inorganic samples are received.

Materials Distilled, June 1964 to June 1965

<u>Name</u>	<u>bp, °C</u>	<u>mp, °C</u>
Durene	196 ⁷ 60	+ 79.3
Methanol	64.7 ⁷ 60	- 97
Nitroethane	114.8 ⁷ 61	- 90
Glycerol	290 ⁷ 60	+ 17.9
<u>cis</u> -Decahydronaphthalene	193.3 ⁷ 60	+ 51
<u>trans</u> -Decahydronaphthalene	185.3 ⁷ 60	- 32
Benzophenone	305.4 ⁷ 60	+ 48.5
Thujaplicin oil	140-150 ₁₄₋₁₅	+ 70
Bromine	58.8	- 7.2
Hydrobromic acid (aqueous)	126	
1,1 dimethylcyclohexane	175	

(R. T. Leslie and E. C. Kuehner)

B. Ultrapure Reagents

1. Scope

Recent advances in trace analysis have created an urgent need for reagents of special high purity because the amount of an impurity sought in a sample is often less than that present in the best grades of reagents normally available. As a result of this urgent need for ultrapurification of reagents to reduce the intolerably high blank corrections, this project was initiated in December 1964. It will eventually include the ultrapurification of many of the reagents and related materials required in the trace analysis activity of the Division, but at present, water, sodium hydroxide, hydrochloric acid, nitric acid, sulfuric acid, and aqueous ammonia have been selected for intensive study with priority being given to water and acids.

The satisfactory storage to prevent deterioration or contamination of the ultrapure reagents by the container is another important problem which is being investigated. This includes a systematic study of various materials from which containers may be fabricated, especially with reference to trace analysis application.

2. Facilities

The methods available for preparing specially purified reagents include distillation, crystallization, zone refining, extraction, and preparative chromatography. However, contaminants introduced into the reagents from apparatus used by these methods are no longer considered negligible and require modifications in techniques. Apparatus and labware require special cleaning techniques or must be constructed from special material to prevent contamination. For example, in the distillation of reagents for the removal of trace metals, a glass still may actually contaminate the distillate by leaching metallic elements from the glass used in its manufacture. Since these metals are more readily leached out by certain acids, it is especially important that the material used in construction of a still for this purpose contain minimum amounts of metallic elements. Because quartz contains less than a tenth as much metallic elements as glass, three of the stills in operation are made of quartz.

When the purification of a reagent or related material is not effective or feasible by the above methods, synthesis will be carried out from reactants which are specially purified.

3. Research and Development

Since the initiation of this project, the emphasis has been on preparing and supplying a few of the most-needed ultrapure reagents and little time has been spent in pure research. Most of the techniques and methods utilized in the preparation of reagents were obtained from literature search and past experiences. Some preliminary research has been started on zone refining of solid sodium hydroxide. The problem of the best container for storing ultrapure reagents will require considerable research and testing. Preliminary work is in progress in preparing ultrapure reagents to be characterized and stored in a number of types of containers.

4. Preparation of Specific Reagents

a. Water. Although water is not a reagent in the strictest sense, it plays an important role in the preparation of proper reagent concentrations. It is, therefore, important that the water used to make up the reagents or used in any other capacity of trace analysis is ultrapurified.

The ordinary distilled water for the Analytical Division staff members located in the Chemistry Building is supplied by a special Barnstead steam-heated still. The evaporator is stainless steel, and the condenser is tinned copper. The still is capable of producing 40 gallons per hour, but is operated at one-fourth that rate to produce water having a conductivity of approximately 4.5×10^{-7} mho. The total metal content in the distillate has not been determined quantitatively; however, an analysis for copper showed 1.5 ppb in water directly from the still and 8.5 ppb in water standing in the storage tanks for 2 weeks. This distilled water does not give a positive result for metals when shaken with chloroformic solution of dithizone unless the impurities are concentrated by a factor of ten by removal of water.

A one-meter, quartz still, shown on the left in figure 24, randomly packed with 4-mm quartz Raschig rings was used for the ultrapurification of ordinary distilled water. This quartz batch still was charged with two liters of the water, and the distillate was collected in three fractions in which only the largest middle fraction was saved. The 50 ml of water allowed to remain in the pot gave a positive test with dithizone-chloroform solution. The pot was then rinsed with a few portions of the middle fraction and charged with the remainder. When this fraction was again distilled in the same manner, no color change was observed when the 50 ml of water remaining in the pot was shaken with dithizone-chloroform solution. This indicated that most of the trace metals were removed by a single distillation in the quartz still having about eight theoretical plates. This test has a sensitivity of about 10 ppb. The

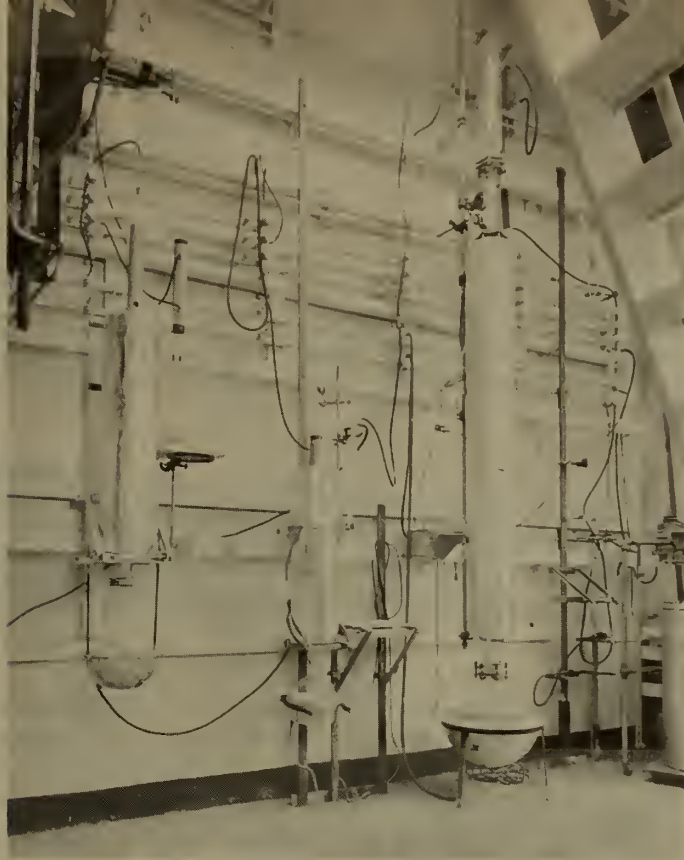


Figure 24. Stills used for preparation of ultrapure reagents.

quartz still described above is being used for the ultrapurification of water until the installation of a continuous distillation quartz still is completed in the proximity of the Barns Barnstead water still. The continuous quartz still will be capable of producing water at the rate of 400 ml per hour which would be sufficient to meet the present demands for specially prepared water. This still would then free the quartz batch still and make it available for the distillation of other reagents.

b. Nitric Acid. A one-meter, all-quartz still (center still in figure 24) which is randomly packed with 4x4-mm quartz Raschig rings is used for the distillation of nitric acid. The still column is lagged with foamed styrene to prevent heat loss and has an estimated efficiency of about eight theoretical plates. The effectiveness of the still in removing trace metals from the reagent under a normal operating procedure was determined. The still pot was charged with 1500 ml and allowed to distill off to dryness at a slightly reduced pressure provided by a water aspirator. The middle fraction containing approximately 1000 ml was collected in a quartz

flask for a second distillation. The still pot was rinsed with 50 ml of specially purified water, and the mixture was shaken with a few drops of chloroformic dithizone solution. A definite color change from blue to pink confirmed the removal of metals in the parts-per-million range. The middle fraction was distilled in a similar manner and the dry pot again rinsed with specially purified water and tested with dithizone. The test revealed only a few parts per billion of metal in the residue and indicates that a single carefully controlled distillation removes most of the trace metals in the reagent grade nitric acid, and a second distillation should produce nitric acid of ultrapurity.

c. Sulfuric Acid. Reagent grade sulfuric acid is distilled in a 60-cm quartz still which is randomly packed with 4x4-mm quartz Raschig rings and lagged with glass wool insulation. Distillation is carried out at reduced pressure provided by an aspirator which serves to remove the initial surge of SO_3 gas released until the azeotrope of H_2SO_4 and water is reached and allows the distillation to proceed at a lower vaporizer temperature. The distillate is collected in three fractions in which the first and last are discarded. The middle fractions from two such distillations are combined and redistilled. The middle fraction from the redistillation is collected in a quartz flask and transferred to a 2-liter quartz container for storing and dispensing.

d. Hydrochloric Acid. At present, specially purified hydrochloric acid is prepared by saturating ultrapurified water with hydrogen chloride gas from a cylinder. The hydrogen chloride gas is first scrubbed by bubbling it through concentrated reagent grade hydrochloric acid before dissolving it in the purified water in a quartz flask.

e. Silica Gel. Silica gel has been included as a material related to reagents since it plays an important role both in purification and in chemical analysis. Metals, especially uranium, were found to be an interfering impurity in a silica gel used in thin-layer chromatography by another section in the Division. A small amount of silica gel was extracted with nitric acid in a Soxhlet extractor in which the gel was contained in three small sintered glass bottom crucibles suspended in a Teflon harness above the siphon drain of the extractor. Nitric acid dripped off the condenser into the top crucible, filtered through the silica gel and glass frit into the crucible below, and eventually reached the lower part of the extractor where it accumulated to a certain level before it siphoned over into the vaporizer. The extraction was allowed to run continuously for 7 days after which the nitric acid was replaced with distilled water. The silica gel was then extracted with distilled water for 2 more days. No quantitative results

on the purity of the silica gel were obtained. However, extraction decreased the impurities by several orders of magnitude to a level where the silica gel was satisfactory for the particular separation by thin-layer chromatography.

Because of the limited capacity of this apparatus, a larger extractor having a 50-g capacity was constructed as shown in figure 25. Condensate from the distillation of nitric acid is forced up through the lower fritted disk and silica gel by hydrostatic pressure. The acid then passes through the upper fritted disk taking along any impurity dissolved in the acid while the silica gel remains in the funnels. Using this apparatus, a 50-g sample of silica gel was extracted with HNO_3 for 3 days and then washed with several portions of specially distilled water. Quantitative determination of the purity of the gel has not been completed; however, preliminary results indicate a considerable decrease of impurities.

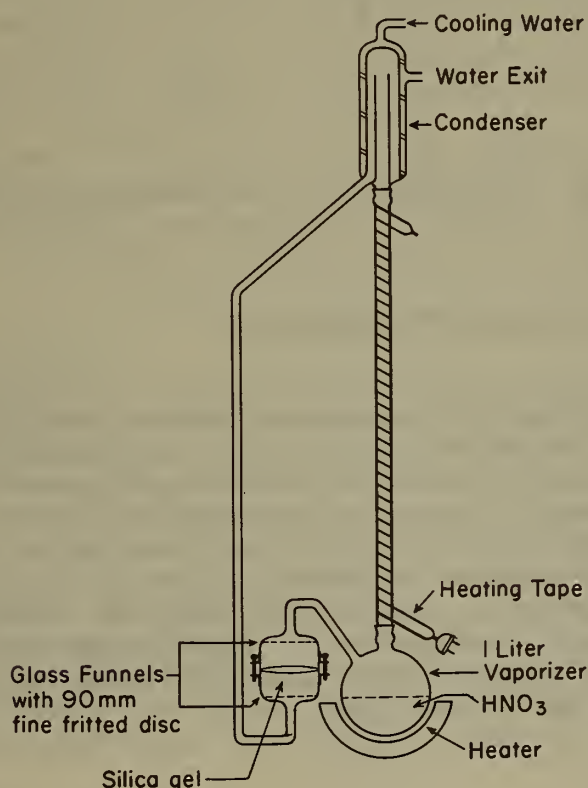


Figure 25. Extractor for purification of silica gel.

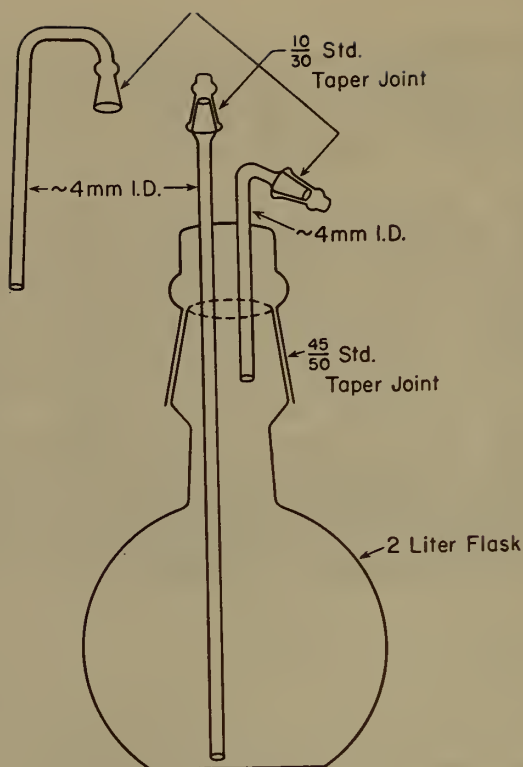


Figure 26. Quartz container for dispensing purified reagents.

5. Use of Ultrapure Reagents

The preparation and distribution of ultrapurified reagents is only beginning to gain momentum since much time has been spent earlier to procure and install the necessary apparatus. In addition to the 50 grams of silica gel previously mentioned, a total of 8 liters of specially purified water and a liter each of ultrapurified nitric acid and sulfuric acid have been provided to staff members of the Division. Also, there is maintained a reserve of two liters each of ultrapurified nitric acid, sulfuric acid, and water. These reagents are stored in and dispensed from two-liter quartz flasks. A sketch of one of them is shown in figure 26.

(E. C. Kuehner)

C. Light-Element Purification

1. Scope

The establishment of accurate values of the physical and thermodynamic properties of solids is often limited by the inability to obtain material that is of high-chemical purity and that is also well-characterized as to its physical state. When such material is not available, large uncertainties are introduced even though compositional determinations are made by the very best analytical procedures and very precise measurements are made of their physical and thermodynamic properties. Generally, inorganic substances are polymorphic, and the solid form of the material can exist in several different crystalline states. In this case, the material to be measured, in addition to a high-chemical purity, must be a solid consisting of only one of the polymorphic forms. Inorganic fluorides are a class of such polymorphic solids of which beryllium fluoride, BeF_2 , was of particular interest at NBS for the ARPA light-elements program.

The main objective of this research was the development of new apparatus, new procedures, and new techniques for physico-chemical phase separations, for chemical purification, and physical-state preparation of pure polymorphs (chemically pure and in one crystalline form) of inorganic fluorides with particular emphasis on beryllium fluoride, BeF_2 . A second very important objective in the planning was the devising of techniques and procedures for the safe handling of inorganic fluorides such as BeF_2 and exclusion of moisture in these processes because of their extreme toxicity at elevated temperatures and their reaction with moisture at ordinary temperatures.

2. Facilities

In January 1962, plans were made to equip a laboratory with facilities for performing phase separations up to 1000°C , whereby inorganic fluorides such as beryllium fluoride could be both chemically purified and prepared as a crystalline product consisting of only one of several possible crystalline forms. A recent photograph (figure 27) shows the physical arrangement of the major facilities in the laboratory. These facilities consist of the following units: Experimental assembly for toxic materials; furnace and temperature control; controlled-atmosphere dry box; special cell for phase purifications; apparatus for the hydrofluorothermal process; and helium leak detector.

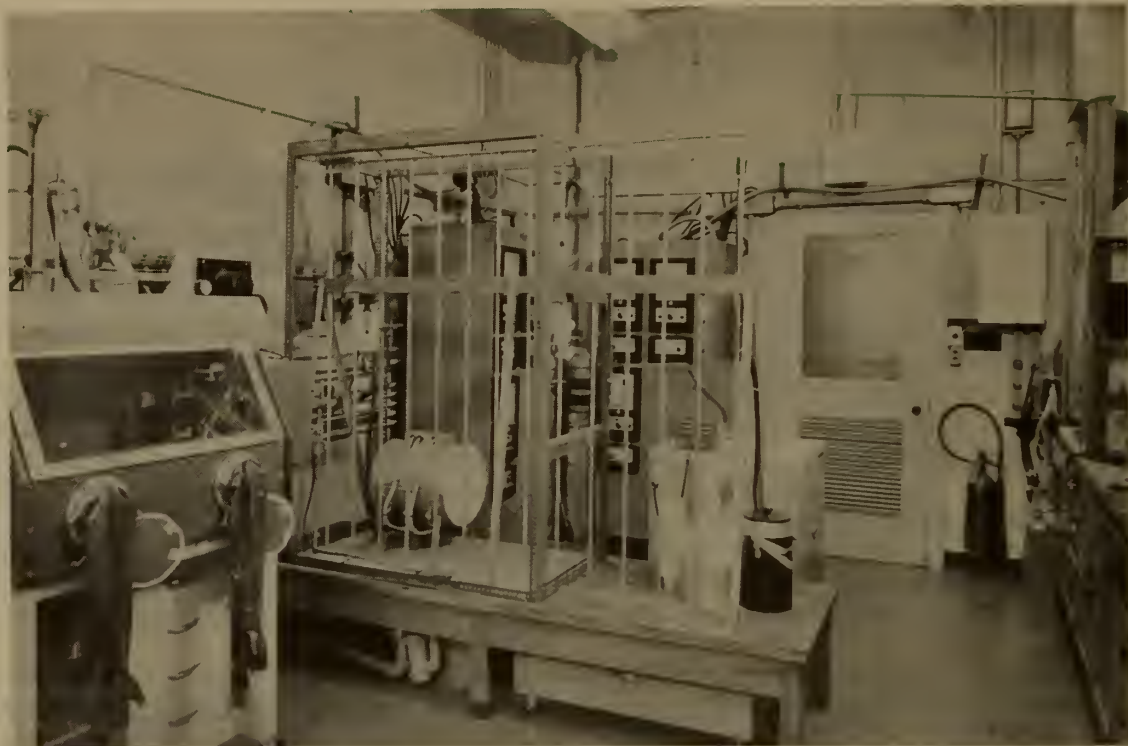


Figure 27. Physical arrangement of the major facilities for light-element purification.

a. Experimental Assembly for Toxic Materials.

For safety in phase purifications up to 1000°C of highly toxic materials, such as BeF_2 , the experimental assembly for closed-system operation has been installed in a three-compartmental manner as shown in the photograph (figure 28).

The high-temperature part of the assembly is in a high-exhaust hood which serves as a separate compartment. The hood is equipped with absolute filters and a 10-foot exhaust pipe on the roof of the building. The hood contained the furnace, the thermocouple leads for recording and controlling the temperatures of three furnace zones, an excess-temperature thermocouple lead for cutting off power to the furnace, three power lines to furnace zones, the experimental vessel, and the upper part of a vacuum manifold of Monel containing a nickel-Monel trap in which by-products that are solids at room temperature are collected.



Figure 28. Three-compartmental assembly for high-temperature experiments with toxic materials.

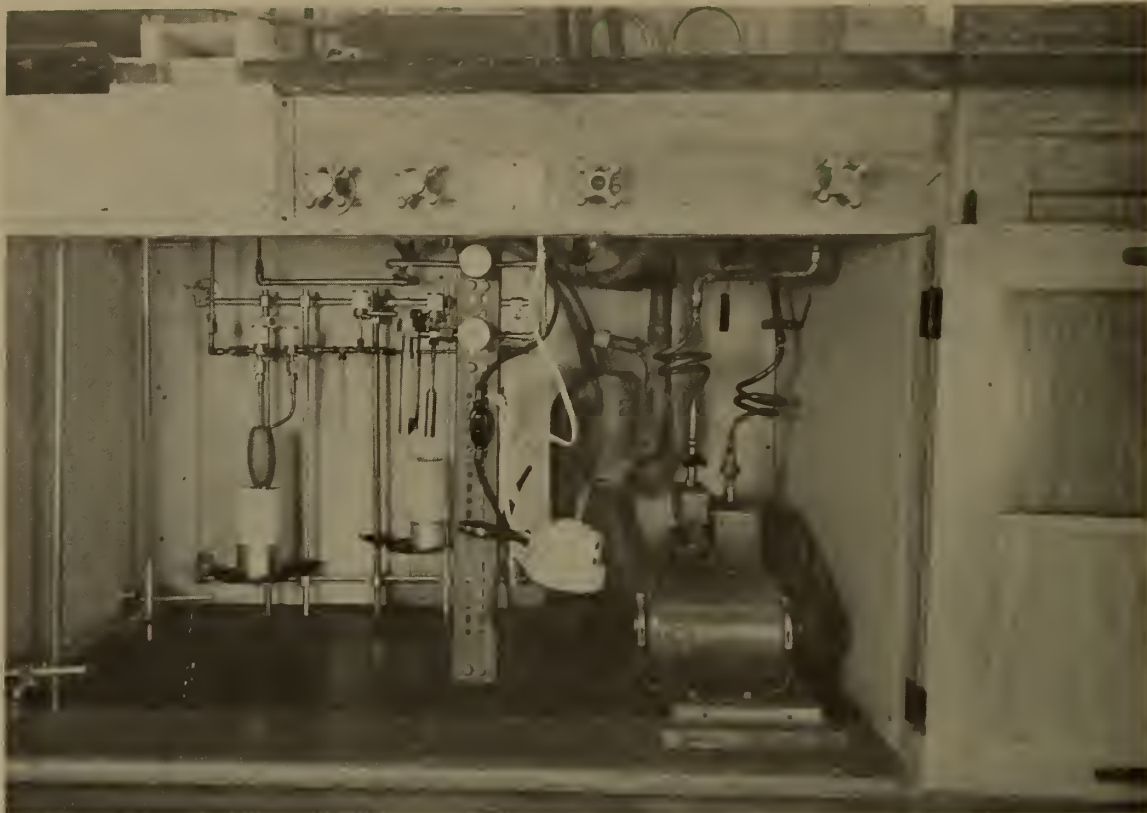


Figure 29. Cabinet area of assembly for low-temperature trap, absorption tube, and fore-pump.

Services for the special cell for phase separations built into the hood proper include: coolant lines to two heat-exchange probes to the cell for condensation of vapors and for nucleation of crystals, six thermocouples for thermal analysis of phase processes in the cell, and two lines for evacuation and pressure control of double-walled, Inconel-nickel spaces of cell.

Another compartment is the cabinet under the hood, in which are located the lower part of the vacuum manifold of Monel (see figure 29), a nickel-Monel trap for liquid and gases, a Monel cylinder for transfer and removal of the trapped liquid and gas, an absorption tube of Monel (for HF vapors with fluorides), and an oil mechanical pump. This cabinet has louvers on the doors, forced ventilation by a small blower into a pipe opening near the exhaust outlet of the hood, and a discharge pipe for the exhaust from the mechanical pump into this same exhaust area of the hood.

A bench area at room temperature, adjacent to the hood, is the third compartmental area on which are located the following: the mercury diffusion pump of glass and the accessories (glass traps and McLeod vacuum gage) for the high-vacuum system proper; a system for evacuation and pressure control of the nickel-Inconel spaces of the body and well of the cell; and a thermocouple assembly with a potentiometer for thermal measurements of six areas of the cell.



Figure 30. Three-zone furnace, automatically controlled, for high-temperature phase separations.

b. Furnace and Temperature Control. A three-zone furnace (figure 30) and a panel cabinet (figure 31) with instrumentation for automatically controlling and recording temperatures as emf of three furnace zones was custom fabricated according to our specifications.

The furnace is of the split-tube type with hinges and a special closing fixture and guide to permit vertical or horizontal operation. The diameter of the shell is $12 \frac{3}{4}$ -inches.

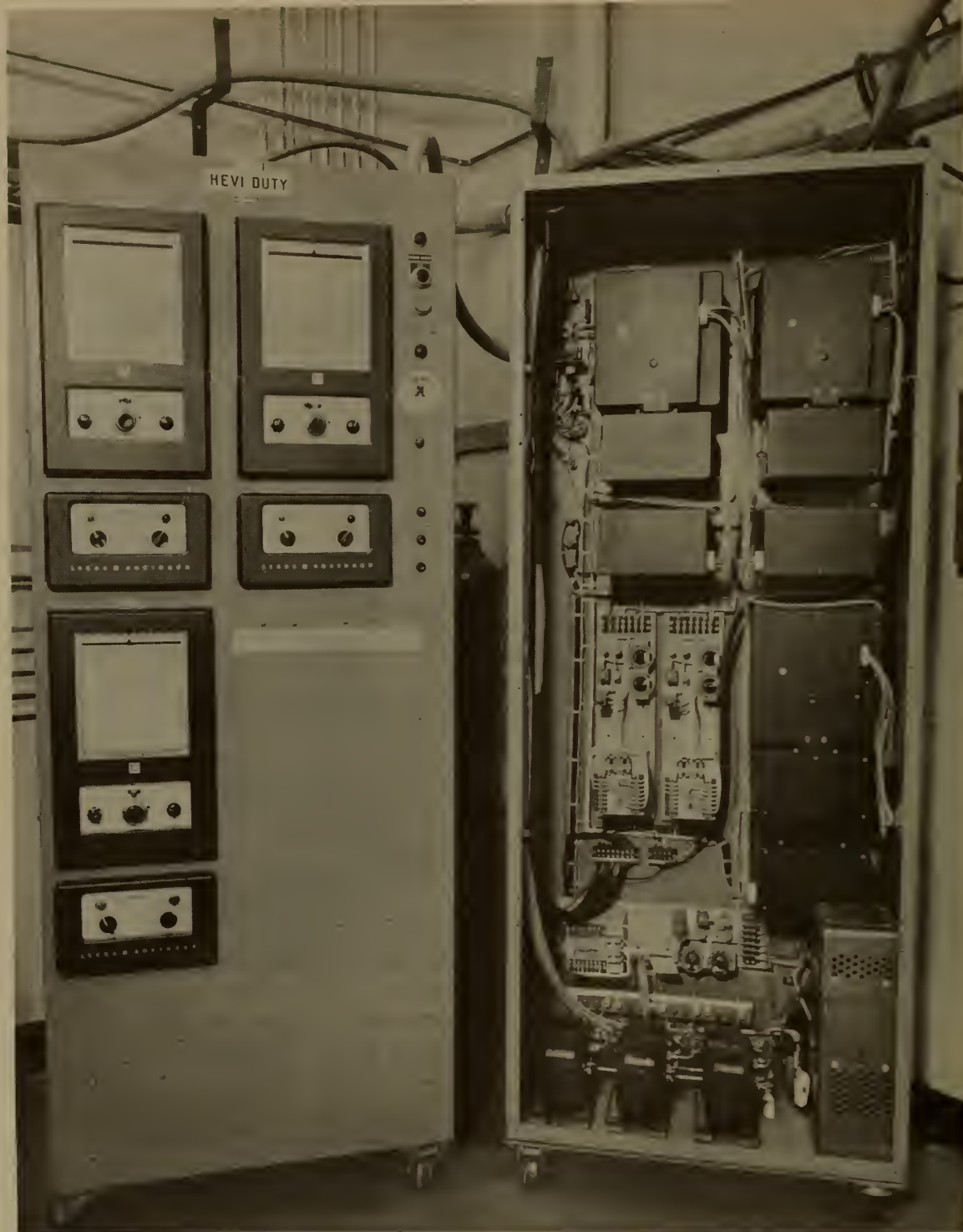


Figure 31. Front and back views of electronic units for automatically controlling and recording temperatures in the three-zone furnace.

The over-all length is 15 1/2-inches with end transite cover plates, 1/2-inch thick, and end vestibules, 1 1/4-inches in length. A type 330 stainless steel liner (2.47-in. i.d. and 2.86-in. o.d.) 14 1/4-inches long fits into the heat chamber. It is held concentric to the heat chamber by the end vestibules and is easily removed. The heat chamber is 12 inches in length and 3 3/4-inches in diameter. It is divided into three electrically heated zones of 4 inches each, which are independently heated with separate power lines to each section. Six chromel-alumel thermocouples are located in the heating elements of the furnace chamber; one in each end zone and four in the center zone. Five of these are used for temperature control and recording. The sixth is used for the over-temperature protection instrument that automatically cuts off power to these zones if the temperature exceeds a predetermined set value.

Thermocouple lead wires from the panel cabinet in a rubber covered cable terminate in a junction box located outside the hood. The six thermocouple leads from the furnace are connected to this box. The electric power cords to each of the three furnace zones are connected to separate power outlets that are located outside the hooded area. The current to these outlets is controlled from the panel cabinet by the emf of the thermocouple in the furnace zone.

Three recorders are used to control and record temperatures as emf for the three furnace zones. The electronic assembly in the panel in addition to the recorders includes three control units, three magnetic amplifiers and self-saturating reactors, one control circuit transformer, one constant voltage transformer, one over-temperature protection instrument, and one main cut-off contactor.

c. Controlled-Atmosphere Dry Box. A controlled-atmosphere dry box with a glove panel and accessories for maintaining a dry, inert atmosphere is used in experimentation with hygroscopic substances, such as BeF_2 . The controlled atmosphere is used in processes involving the filling and removal of material into or from the experimental vessel.

The glove box (figure 32) is basically a commercial model with the exception that, in addition to the interchange compartment on one end, there is also a swinging door panel on the other end which is used for inserting large experimental vessels.

Main alterations in the box include the following: a well for the special cell so that it may be assembled or disassembled in a vertical position; a line, gauge, and vacuum

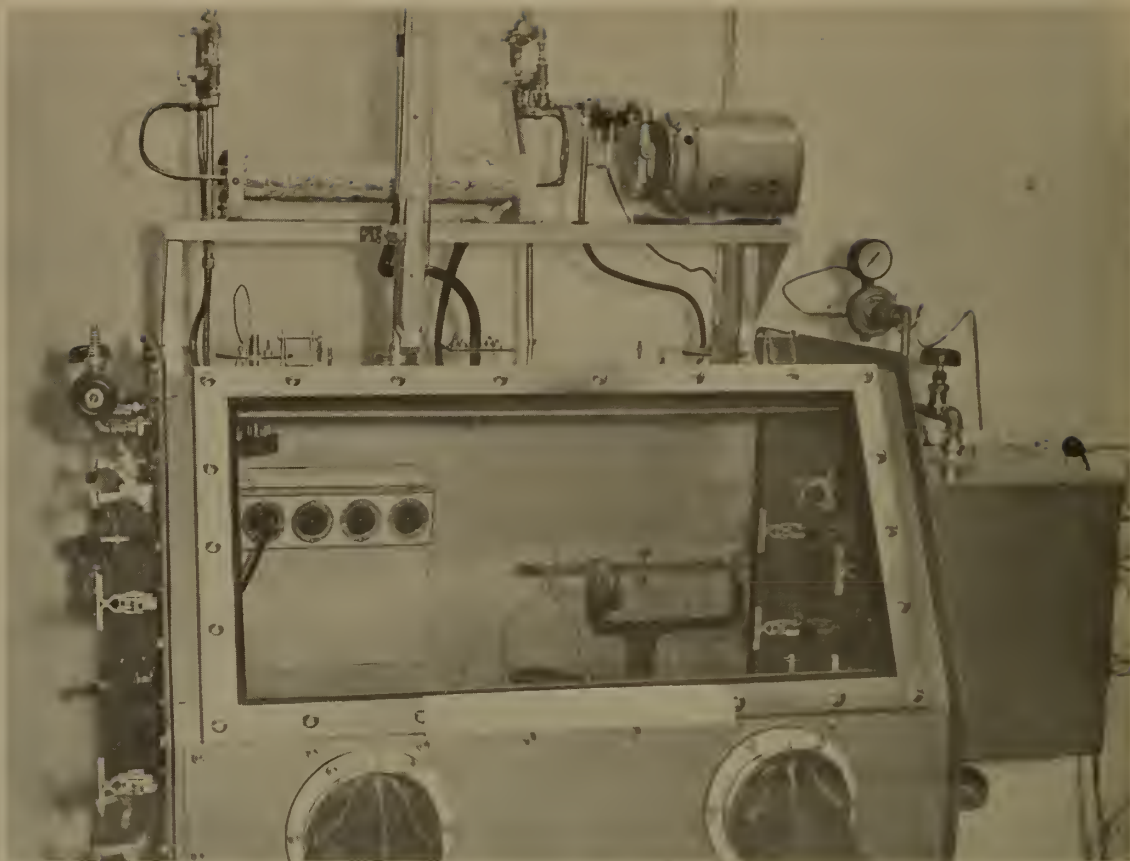


Figure 32. Controlled-atmosphere glove box.

pump for the evacuation and subsequent filling of the interlock compartment with an oxygen-free, moisture-free gas such as nitrogen; metal drying tubes packed with molecular sieves which may be reactivated in place; a line to discharge the pressure release from the circulating pump into the box rather than into the room; two manifold lines which connect the valves to a gas inlet system through a pressure gauge or a gas outlet system that is connected through one union coupling to a line to the hood such that all gases are vented to the hood; and a dew-point device for sensing the moisture content of the box.

d. Special Cell for Phase Purification. A cross-sectional drawing of the special cell, that was designed and constructed at NBS, for use to 1000°C in phase purifications and thermal analysis for the preparation of pure crystalline polymorphs of polymorphic inorganic fluorides is shown in figure 33. The numbers in the figure refer to the disassembly

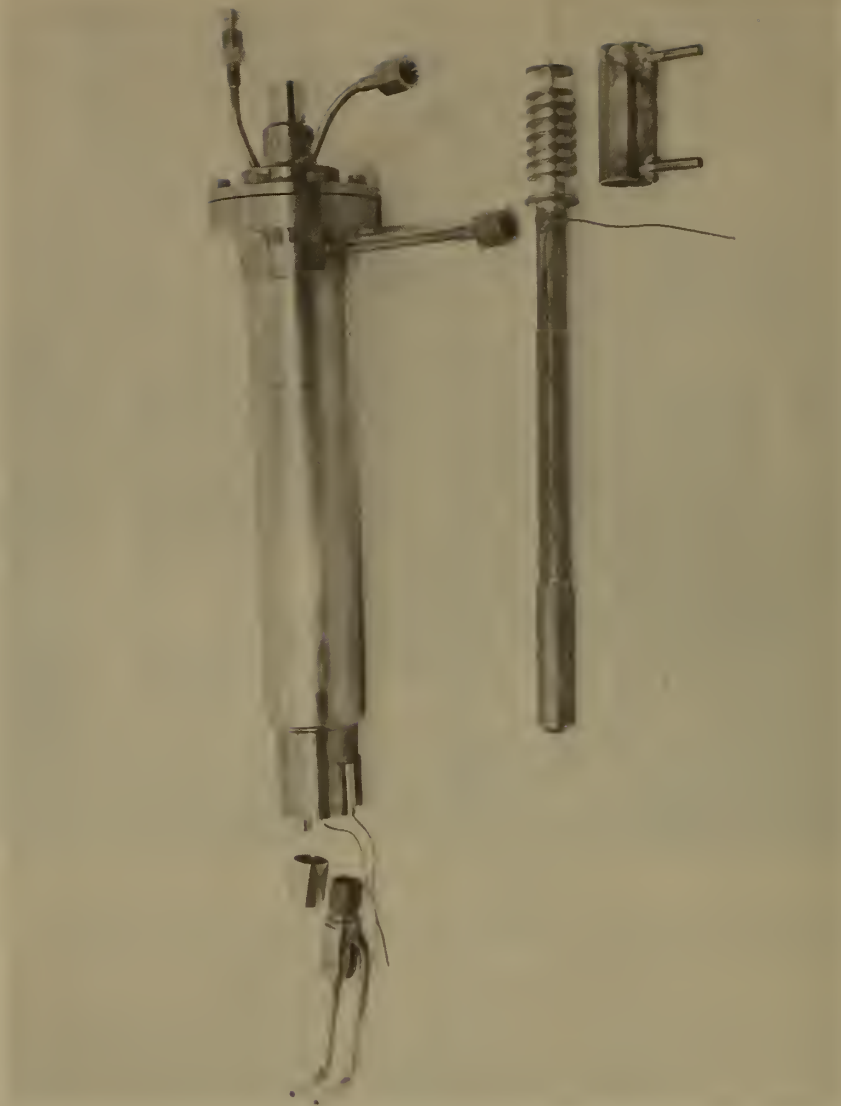


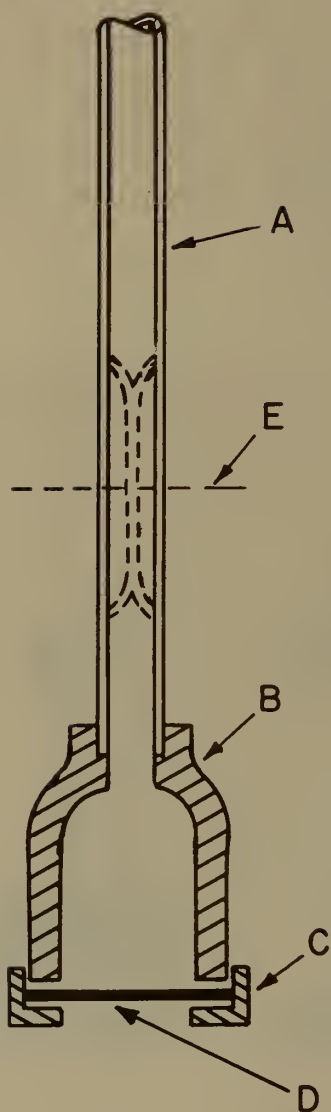
Figure 34. Assembled cell for use at 1000°C in phase purification.

parts, the lower case letters to welds, and the capital letters to details of other parts. Photographs of the assembled and disassembled cell are shown in figures 34 and 35. Figure 34 also shows two heat-exchange probes that are used for the removal of heat at re-entrant coolant well, B, and at protrusion, M, of the cell for crystal nucleation. Figure 35 shows the tool for removing vessel 6 by interlocking into grooves J.

The cell is provided with removable containers at the bottom, lower center, and top of the cell in which the products as solids can be removed after phase separations involving distillation, crystallization, sublimation, and preferential decomposition. These operations are performed in a hooded area with the cell placed in a vertical position in a three-zone control furnace whose temperatures are automatically controlled and recorded by remote electronic controls. A closed stopcock at A protects the contents of the cell after pretreatment or phase separations. Disassembly of the cell for filling or product removal is performed in the dry box.



Figure 35. Disassembled cell for use at 1000°C in phase separations.



- A. Platinum tube 1/8 inch o.d., 0.010 inch wall
- B. Platinum-iridium body (90% Pt-10% Ir alloy)
- C. Platinum-iridium ring (90% Pt-10% Ir alloy)
- D. Platinum disk, foil 0.001 inch thick soldered to B and C
- E. Position where tube is cut off after filling with HF and closing tube with pliers.

Figure 36. Rupture-disk ampoule.

e. Apparatus for the Hydrofluorothermal Process.

A cross-sectional drawing of the rupture-disk ampoule for the anhydrous addition of hydrogen fluoride to a closed bomb is shown in figure 36. This ampoule was designed for use in the development of a method for the hydrofluorothermal growth of BeF_2 crystals under HF pressure similar to the hydrothermal growth of quartz from SiO_2 . Photographs of the manifold used to fill the ampoule and the platinum-lined Morey bomb and parts are shown in figures 37 and 38.



Figure 37. Manifold used to fill rupture-disk ampoule.

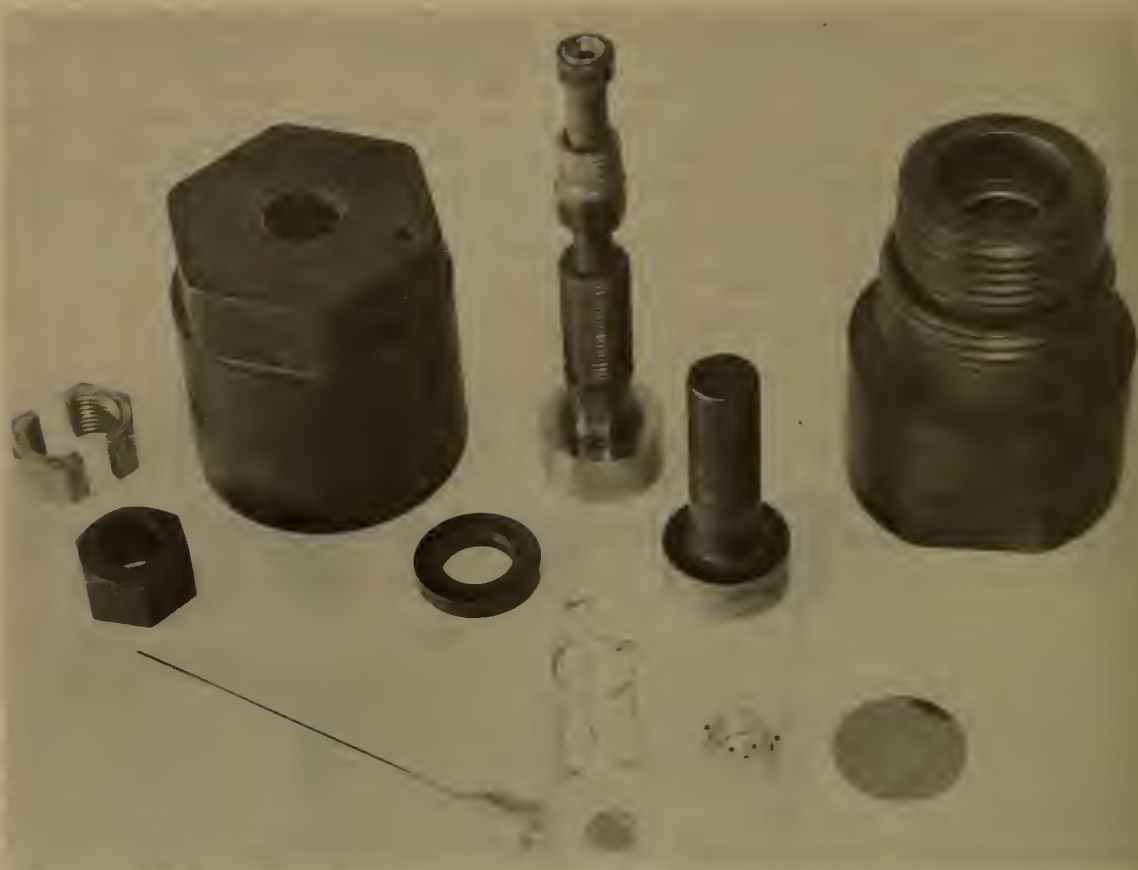


Figure 38. Platinum-lined Morey pressure bomb and parts.

f. Helium Leak Detector. The mass spectrometer leak detector is capable of detecting one part of helium in 10 million parts of air or leaks of 10^{-10} cc per second. Metal parts and assemblies in this research are tested for tightness with this detector.

3. Evaluation of Performance

a. Experimental Assembly for Toxic Materials. The three-compartmental arrangement of the experimental assembly has been used successfully in filling ampoules with HF gas for the hydrofluorothermal process and in performing phase separations to 1000°C with BeF_2 in the special cell.

The above compartmental arrangement of the experimental assembly has the following advantages. The separation of the most hazardous, high-temperature part of the apparatus from the others minimizes danger in that only a few operations at most or none at all are required in this area during an experiment; whereas, in the cabinet area, frequent attention is required in the refrigeration with liquid nitrogen of the trap for liquid and gas and in the transfer of the trap contents to a cylinder. Also in the case of a failure in the experimental vessel at the high temperature, the vacuum manifold in the hood can be isolated from the vacuum system by closing a valve in the cabinet area. The location in another area of the glass system that was available for producing and measuring a high vacuum, facilitates the much more frequent attention to this part of the system. Further, it separates the glass parts containing mercury in the diffusion pump and in the McLeod gage from the all-metal system within the hood and cabinet areas, thus minimizing breakage and enhancing safety.

In setting up a laboratory for high-temperature research with toxic materials, alterations were made in an existing hood to achieve the above separations of the apparatus assembly into three areas. However, commercially available hoods designed on this principal would appear to be of a great advantage to other workers performing experiments with toxic materials at high temperatures under high-vacuum and controlled-pressure conditions.

Description and drawings of the trap, the ultrahigh vacuum couplings of Monel, and the high-temperature valve of nickel and Monel, which are used in the manifold, have been reported [20]. A description of the high-temperature valve will be prepared for formal publication [21].

b. Furnace and Temperature Control. The custom design and automatically controlled three-zone furnace [22] has performed well in establishing and reproducing varied heat environments that are required to achieve the experimental heat conditions in the furnace for performing different types of phase separations to 1000°C in the special cell.

The thermocouples for controlling and recording the temperatures of the three furnace zones are arranged so that each zone may be operated independently or with either end zone as a slave to the center zone. Temperature control with this system was such that the band width on the strip chart of the recorder for the center zone was constant to within several hundredths of a degree in the range of 500 to 1000°C when the end zones were operated as slaves to the center zone.

c. Controlled-Atmosphere Dry Box. The modified glove box, described under facilities, has been operated under a good anhydrous atmosphere as sensed by dew-point readings below -80°C , and in some cases after long periods (one week), below -165°C .

The balloon inflation and deflation technique allows the air in the main portion of the box to be displaced and filled with a controlled atmosphere such as nitrogen. The interlock compartment can also be conditioned to a controlled atmosphere by provisions made for its evacuation and subsequent filling with a dry gas.

The special panel door allows large objects such as a vacuum desiccator or the special cell to be placed in the box without any panel disassembly. The well, built in the bottom of the glove box, allows the special cell to be housed in a vertical position for its assembly or disassembly during fillings or product removals.

d. Special Cell for Phase Purifications. The fabrication of the inner system of the cell for resistance to chemical attack, the machine design for optimum heli-arc welds with no crevices for a noncorrosive surface and a vacuum-tight seal, and the provisions for thermal analysis and for the detection of temperatures for phase separations and polymorph formation have been tested to be quite satisfactory in operations of the cell to 1000°C with BeF_2 . Details of the cell fabrication, cell design, thermal analysis during phase purifications, and the varied phase separations involving distillation, crystallization, sublimation, and preferential decomposition will be described in a formal publication [23]; for other reports see [24, 25, 26].

In the program for the chemical purification and chemical analysis of BeF_2 , and its preparation as a pure crystalline solid of only one of the polymorphic forms, the following tasks have been achieved by phase separations in the special cell: (1) a more accurate analysis of the BeO content in the original sample of BeF_2 through analysis for BeO in the residue portion after distillation [27]; (2) chemical purification of BeF_2 by distillation in vacuo to remove volatile impurities to concentrate BeO in residue, and to condense BeF_2 vapors as a glassy solid of high-chemical purity [28]; and (3) the preparation of BeF_2 in vacuo and collection of its vapor product as a well-defined, crystalline solid, which after cooling and removal at room temperature in a dry box, was identified as a single polymorphic species, alpha (low temperature), quartz-like, hexagonal form of BeF_2 [28].

The pure crystalline polymorph of BeF_2 described above fulfills the material requirements of a high-purity, well-defined, crystalline solid sought for in the establishment of very reliable physical and thermodynamic properties for BeF_2 in the ARPA light-elements program. The amount on hand, however, is small with the major portion of the distillate obtained as a glassy solid. However, different temperature conditions for the condensation of the vapors would be expected to enhance the yield of the major portion of the distillate as the crystalline product and thus offers a good method for producing the large quantity (150 g) of a pure crystalline polymorph of BeF_2 . The glassy BeF_2 of high-chemical purity and free of gaseous or other inclusions is also very useful for other aspects of the program such as determination of the vapor pressure and heat of fusion. Another possible use for this material would be as a chemical standard for beryllium and/or fluorine.

e. Apparatus for Hydrofluorothermal Process. A major bottleneck in the development of this process has been the anhydrous addition of HF to a closed bomb. The technique for this addition from a rupture-disk ampoule (figure 36) was perfected. The manifold used for the transfer of gaseous HF from the cylinder to the ampoule is shown in figure 37 and the bomb parts are shown in figure 38. A short formal publication of this technique is planned [29]; for other reports see [30, 31].

(A. R. Glasgow, Jr.)

D. Other Purification Techniques

In the past, considerable use has been made of a variety of physical methods for separating materials. Liquid-liquid extraction, especially with low-boiling solvents (below 0°C) which are easily removed, and solid-liquid absorption (chromatography), using low-boiling elutants, have been used. Adduct and clathrate formation have been applied occasionally. Low-temperature solubility differences have also been found to be useful (for example, a cold solution of hydrocarbons in liquid propane partially precipitates when poured into liquid methane). Any of these methods can be reactivated if their use is indicated.

Currently the section is prepared to purify some materials by multiple zone melting of solids, very slow freezing of liquids (directional freezing), or preparative gas-liquid chromatography.

Quantities of about 10 g or less of materials which melt between about 50° and 150°C can be zone melted in sealed tubes by external resistance heaters which traverse the tube automatically. Quantities of 0.5 to 1.5 liters of materials which freeze between about $+50^{\circ}$ to -150° can be purified by directional freezing. The freezing is done by very slow cooling in a spherical, vacuum-jacketed container of glass which is submerged in a bath slightly cooler than the freezing point of the material. The liquid phase is stirred during the freezing by swirling the entire apparatus in the bath, first in one direction and then in the opposite direction, for about 10 revolutions at the rate of about 30 revolutions per minute. A thermocouple and a resistance thermometer placed in a well which is located in the axis of rotation permits recording of the temperature.

A gas-liquid chromatograph with a column 5/8-inch in diameter by 12 to 60-feet long is available for some separations on a macro scale by this method. In its present state, the apparatus is most suited to separating materials which boil below 100°C . Automatic injection of samples and programed collection of product can be arranged, but hand injection of about 2-ml samples and personal attention to the collection of product has been used for most separations.

(R. T. Leslie)

3. PERSONNEL AND ACTIVITIES

A. Personnel Listing

John K. Taylor, Section Chief

Elaine H. Beale, Secretary

CHEMICAL ANALYSIS

Mass Spectrometric Gas Analysis --

Ernest E. Hughes, William D. Dorko

Polarography --

E. June Maienthal

Coulometry --

George Marinenko

Microchemistry --

Rolf A. Paulson, Robert J. Hall

Stoichiometry --

Thomas J. Murphy

Cryoscopy --

Herbert D. Dixon

PURIFICATION

Distillation --

Robert T. Leslie

Ultrapure Reagents --

Edwin C. Kuehner

Light-Element Purification --

Augustus R. Glasgow, Jr.

B. Publications

1. E. J. Maienthal and J. K. Taylor, Separation and determination of zirconium in zirconia-yttria mixtures by precipitation with cupferron, Anal. Chem. 36, 1286 (1964).
2. H. R. Finegold, NMR studies of asymmetric ethanic rotators: 1,2-disubstituted propanes, J. Chem. Phys. 41, 1808 (1964).
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7. J. K. Taylor and G. Marinenko, High-precision coulometric analysis with special reference to the determination of uranium, Proc. Conf. High-Precision Anal. Substances of Interest to Nuclear Energy, p. 147, EURATOM, Bureau Central de Mesures Nuclaires, Brussels (January 18-22, 1965).
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11. R. T. Leslie and E. C. Kuehner, Distillation analysis Encyclopedia of Chemistry, Reinhold, N.Y. -- In Press
12. E. C. Kuehner and R. T. Leslie, Sublimation, Encyclopedia of Industrial Analysis, Interscience, N.Y.-- In Press
13. J. K. Taylor, Density and specific gravity, Encyclopedia of Industrial Analysis, Intersciences, N.Y. -- In Press

14. A. T. Horton, A. R. Glasgow, Equipment for single-crystal growth from the melt suitable for substance with a low melting point, J. Research NBS (Phys & Chem) -- In Press
15. J. K. Taylor, E. J. Maienthal, and G. Marinenko, Electrochemical methods, Trace Analysis, Intersciences, N.Y.-- In Press
16. R. T. Leslie, Distillation as a tool for purification of research quantities of materials, Ann. N.Y. Acad. Sci. -- In Press

C. Talks

1. A. R. Glasgow, Jr., "Rupture-Disk Ampoule for Anhydrous Addition of HF to a Closed Bomb," 19th Annual Calorimetry Conf., NBS-Naval Med. Res., Washington, October 1964.
2. A. R. Glasgow, Jr., "Thermal Analysis in Phase Purifications of Polymorphic Solids," Anachem Conf., Detroit, October, 1964.
3. J. K. Taylor, "Electrical Measurements and Chemical Analysis," Science Club, Rollingcrest JHS, December 1964.
4. J. K. Taylor and G. Marinenko, "High-Precision Coulometric Analysis with Special Reference to the Determination of Uranium," EURATOM Conf., Brussels, January 1965.
5. J. K. Taylor, "Standards of Measurement," American Univ. Teachers Institute, February 1965.
6. G. Marinenko and J. K. Taylor, "Coulometric Calibration of Microvolumetric Apparatus," Pittsburgh Conf. on Anal. Chem. and Appl. Spectroscopy, Pittsburgh, March 1965.
7. E. J. Maienthal and J. K. Taylor, "Determination of Tellurium in Spectrographic Cartridge Brass and White Cast Iron Standards by Cathode-Ray Polarography," Pittsburgh Conf. on Anal. Chem. and Appl. Spectroscopy, Pittsburgh, March 1965.
8. R. T. Leslie, "Distillation as a Tool for Purification of Research Quantities of Material," Conf. on Purification of Materials, N.Y. Acad. Sciences, N.Y., May 1965.
9. E. E. Hughes and W. D. Dorko, "High-Pressure Mass Spectrometry for Trace Analysis with an Analytical Mass Spectrometer," Am. Chem. Soc. Meeting-in-Miniature, Baltimore-Washington Section, Univ. Md., College Park, May 1965.
10. G. Marinenko and J. K. Taylor, "Precise Analysis of Uranium by Constant-Current Coulometry," Am. Chem. Soc. Meeting-in-Miniature, Baltimore-Washington Section, Univ. Md., College Park, May 1965.

D. Committee Activities

J. K. Taylor

Service Analysis Coordinator, Analytical Chemistry Division
Member, Analytical Standards Committee
Chairman, Panel on Chemistry, Civil Service Board of Examiners
Vice-Chairman, Civil Service Board of Examiners

Member, Review Board, Science Book List, American Association
for the Advancement of Science

President-Elect, Washington Academy of Sciences (WAS)

Chairman, Committee on Science Education, WAS

Member, Joint Board on Science Education

Director of Science Projects

Elected member, Council of the American Chemical Society (ACS)

Member, Canvassing Committee for the ACS Award in Pure Chemistry

Member, Advisory Board, Analytical Chemistry, journal of the ACS

Secretary-Treasurer, ACS Division of Analytical Chemistry

Chairman, Analytical Topical Group, Chemical Society of Wash-
ington

Member, Board of Managers, Chemical Society of Washington

Member, Professional Relations Committee, Chemical Society of
Washington

Chairman, Publicity Committee, Electrochemical Society

Session Chairman, 1965 Eastern Analytical Symposium

E. C. Kuehner

Coordinator, Ultrapure Reagents Committee, Analytical Chemistry
Division

E. June Maienthal

NBS Reporter for Capital Chemist, Chemical Society of Washington

Elected member, Board of Managers, Chemical Society of Washington

T. J. Murphy

Member, Civil Service Board of Examiners

Member, Committee on Meeting Arrangements, Chemical Society of
Washington

R. A. Paulson

Member, Service Analysis Committee, Analytical Chemistry Division

Collaborator on the Committee for Study of Microchemical Methods,
Association of Official Agricultural Chemists

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- [22] A.R. Glasgow, Jr., Design of automatically controlled, high-temperature, three-zone furnace, J. Res. NBS (Eng&Inst). To be prepared for publication.
- [23] A.R. Glasgow, Jr., Preparation of pure crystalline solids by phase purifications at high temperatures, J. Res. NBS (Phys&Chem). To be prepared for publication.
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